CONTROLLING DIFFUSION FOR RAPID FORMATION OF INTERCONNECTS

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Presented by

Karolina Krystyna Sobol
(née Sosnowska)

M.Sc. Eng., Warsaw University of Technology

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citizen of

Poland

accepted on the recommendation of

Prof. Ralph Spolenak ( Examiner)
Prof. Jolanta Janczak-Rusch ( Co-examiner)
Prof. Peter Uggowitzer ( Co-examiner)
Prof. Wolfgang Tillmann ( Co-examiner)
There's more to life than books, you know. 
But not much more.

~ The Smiths ~
Abstract

The application of wide band-gap semiconductors enables a significant increase of service temperatures of power modules. However, a rapid interconnects technology that would withstand such severe thermal conditions and meet the requirements of the Restriction of Hazardous Substances Directive is still missing. The method of Transient Liquid Phase (TLP) bonding represents one such promising alternative. The TLP bonding is based on isothermal solidification and allows formulating thermally stable, cost effective bonding, if the atomic mass transport can be controlled.

Through the course of this research, it has been shown that the control of atomic diffusion affects the solid-state reaction between Cu and Sn, and the formation of the intermediate phases between them. The control over the mass transport was postulated and achieved through two methodological approaches – blocking or enhancing the solid-solid reaction. The inhibition of solid-solid interaction was realised through process conditions – rapid heating rates in conventional TLP bonding, and through the incorporation of a temporary diffusion barrier coating – Sacrificial Passivation. The exploitation of solid-solid reaction was realised through the architecturing of nano-multilayers and the provision of intimate contact between the thin films of Cu and Sn.

It was elaborated that heating rates of at least 350 °C/min change the bond formation mechanisms and limit solid-state IMC growth. The initial interfacial IMC layer is much thinner and allows for quick interfacial transport of the diffusive species (mainly Cu) that supersaturate and initiate IMC nucleation and growth within liquid Sn. The overall time required for IMC formation during isothermal solidification is then shortened. Sacrificial Passivation, in the form of thin organic film, was seen to preclude the early solid-state interdiffusion, but still allowing the subsequent liquid phase reaction to proceed upon heating. The thermally driven deactivation of the Sacrificial Passivation was achieved for Cu and Ag (as reference). The coating successfully steered the interfacial reaction between Ag/Sn, was however less effective for the Cu/Sn. The controlled use of reactive diffusion in a solid-state between Cu-Sn was demonstrated on a nano-architectured multilayer system. The scaling criteria were established to provide control over IMC phase formation. Size effects in the phase formation in Cu-Sn nano-multilayers were observed with the three regimes of the phase formation
(nano-regime at 20 nm, transition at 50 nm and bulk-like above 100 nm). At the nano-regime a δ-Cu$_{41}$Sn$_{11}$ intermetallic phase was found instead of typically seen in bulk the η-Cu$_6$Sn$_5$, regardless of the initial sample composition. The thermally driven redistribution of phases for the nano-regime did not follow the bulk behaviour either, suggesting that driving forces for the thermodynamics are affected by the extensive number of interfaces and their energy present in the system. These interfaces can be designed to provide fast diffusion paths for enhancing reaction rates at low temperatures. Presented discovery supports the targeted development of nano-architected materials for microelectronic assembly.

The formulation of methodologies to control reactive diffusion in Cu-Sn was experimentally demonstrated and the fundamental understanding of the mechanisms governing the behaviour achieved. With these results, current work pushes the frontiers of the microelectronic packaging towards the rapid formation of interconnects.
Zusammenfassung


Dabei wurde gezeigt, dass sich der Mechanismus bei hohen Heizraten von mindestens 350 °C/min insofern ändert, dass die Verbindung und das Wachstum der Festkörper intermetallischen Phase (intermetallic compound, IMC) limitiert sind. Die zu Beginn vorhandene intermetallische Schicht an der Grenzfläche ist sehr dünn und ermöglicht daher einen raschen Transport in die Nachbarschicht, welche sich in der Folge rasch mit Cu übersättigt, was wiederum zu Keimbildung
und Wachstum von intermetallischen Verbindungen im flüssigen Sn führt. Somit verkürzt sich die Gesamtzeit, welche zur Bildung und isothermen Erstarrung der IMC Schicht erforderlich ist, deutlich. Sacrificial Passivation erreicht man beispielsweise durch das Aufbringen von dünnen organischen Filmen, welche die frühe Festkörperdiffusion hemmen, aber zu einem späteren Zeitpunkt beim Erhitzen plötzlich in die flüssige Phase übergehen und somit auf einen Schlag von der Grenzfläche verschwinden. Die thermisch induzierte Deaktivierung einer organischen Schicht wurde am Modellbeispiel Cu/Sn gezeigt, war aber weniger ausgeprägt als im Kontrollsystem von Ag/Sn. Dafür wurde die präzise Kontrolle von reaktiver Diffusion im festen Zustand im Cu-Sn System am Beispiel von nanostrukturierten Multischichtsystemen gezeigt. Zur Auswertung wurden Skalierungskriterien festgelegt, welche die Kontrolle über IMC Phasenbildung vereinfachten. Größeneffekte bei der Phasenbildung in Cu-Sn Nanomehrfachschichten in drei Bereichen (Nanobereich unterhalb um 20 nm, Übergangsbereich um 50 nm und festkörperähnliche Eigenschaften oberhalb von 100 nm) beobachtet. Der Nanobereich förderte zunächst eine δ-Cu_{41}Sn_{11} Phase zutage anstelle der erwarteten η-Cu_{6}Sn_{5} und zwar unabhängig von der anfänglichen Probenzusammensetzung. Die thermisch angetriebene Phasenänderung ist im Nanobereich unterdrückt und entspricht klar nicht dem Festkörperverhalten, was wiederum darauf hindeutet, dass die treibenden Kräfte für die Thermodynamik durch deutlich höhere Grenzflächenenergien ausgehebelt werden. Grenzflächen können also speziell so verändert bzw. konzipiert werden, damit sie kurze Diffusionswege für erhöhte Reaktionsgeschwindigkeiten bei niedrigen Temperaturen bereitstellen. Diese Entdeckung unterstützt die zielgerichtete Entwicklung von metallischen Nanomaterialien und deren massgefertigten Einsatz in mikroelektronischen Bauteilen der Zukunft.

Zwei Methoden zur Beeinflussung der reaktiven Diffusion wurden im Modellsystem Cu-Sn experimentell aufgezeigt und die dabei zugrunde liegenden Mechanismen untersucht und bzw. bestätigt. Die dabei gefundenen Ergebnisse tragen entscheidend zur Weiterentwicklung in der Verbindungstechnik in Halbleiter- und Mikroelektronikindustrie bei.
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Part 1. Introduction
Chapter 1. Background motivation

The fundamental achievements of the past decade in R&D of semiconductor materials compromise the excessive demands for the tomorrows' highly efficient power electronic modules. The application of wide band-gap semiconductors enables a significant increase of service temperatures of power modules. However, a short-duration packaging technology (so called die-attach) that would withstand such severe thermal conditions and herewith not conform Restriction of Hazardous Substances Directive (RoHS) directives is still lacking. Addressing the issue of rapid formation of interconnects that compromise processing requirements of the power module packaging is of immediate relevance given that few world-player, like ABB Semiconductors or Siemens are currently applying wide-band semiconductors in their commercial offerings, still using high-Pb bearing solders.

Hereby, presented work delivers scientifically justified approach to involve diffusion phenomena occurring at the nano-scale, as the answer to this call. Using low cost materials, the adequate control of interdiffusion is poised to formulate the process allowing in the end a short time, low temperature interconnects formation. This work, is focused onto design and description of kinetically or thermodynamically reasoned diffusion steering mechanisms providing control over interdiffusion reaction between the joining components. This control is realised either through hindering or exploiting solid-state diffusion, thus allowing the rapid interconnect formation, what has been confirmed experimentally.
Chapter 2. State of the art

The diffusion processes have a significant importance for diverse technological applications, i.e. surface hardening of steel, solid electrolytes for batteries and fuel cells, doping during fabrication of semiconductors, as well as for an interfacial reaction during sintering and joining processes [1].

The diffusion in joining process is particularly critical for microelectronic assembly, both in the segment for consumer, and for power electronics\(^1\). The typical microelectronic assembly process is called die-attach.

The die-attach procedure provides mechanical, thermal, and electrical connection between the power module and the support. The current industrial procedure to fix a semiconductor chip onto the package is realized through the conventional soldering process [4]. This process is divided into three stages: (i) heating to melt solder material; (ii) solid-liquid interaction at processing temperature between solder and base material; (iii) final joint solidification through cooling.

Fig. 1.1 gives a schematic overview on temperature regimes for joining \((T_{\text{bond}})\) and operation \((T_{\text{work}})\) of the components used in consumer \((T_{\text{bond1}}, T_{\text{work1}})\) and power electronics \((T_{\text{bond2}}, T_{\text{work2}})\), as well as a solution technique binding these two temperature sets together. For the assembly of wide band-gap semiconductors conventional lead-free solders remit at the operational temperatures of these devices. The available solders with enough high thermal conductivity and creep resistance are either expensive (i.e. 97Au-3Si88Au-12Ge and 80Au-20Sn) or environmentally hostile, diverging from ROHS directives (i.e. 97.5Pb-1Sn-1.5Ag). Hence, none of them is fully satisfactory. A resolving solution could be an alternative packaging approach that would use low melting point interconnecting material, but yet provide high temperature operations of the device.

\(^1\) Power electronics is part of electrical engineering dealing with efficient conversion, control and modification of the flow and form (i.e. voltage or current) of electrical energy between available inputs of the power into the desired electrical output [2]. Technologically, it is based on solid-state electronics operating at power levels ranging from 0.1 to over 1 MWatts. In the respect of the raising demands on miniaturization and high efficiency of power modules, the Si-based devices are reaching their limits of operating frequency, breakdown voltage, and power density [2]. Recently, the industrial focus has been shifting towards promising alternatives, so called wide band-gap materials, like AlN, GaN or SiC that could operate at high temperature and high power switching applications [3]. Those trends set up even harsher requirement towards joining technologies for power electronics.
Fig. 1.1 – Schematic overview of temperature requirements for different die-attach materials and their applications. The blue and red regions reflect typical operation temperatures for respectively, consumer and power electronics products, with marked functional temperature for wide band-gap semiconductors. The area below the temperature axis indicates the materials and their processing temperatures – for low melting point die-attach solders (green coloured region), and high melting point die-attach solder alloys (yellow coloured region). For die-attach of wide band-gap semiconductors, the solders used require high thermal conductivity and creep resistance. Such solders are either high Au-bearing (expensive) or high Pb-bearing (not environmentally friendly).

The method of Transient Liquid Phase (TLP) bonding represents one such promising alternative. The TLP bonding is based on isothermal solidification and allows formulating thermally stable, cost effective bonding, if the atomic mass transport can be controlled.

2.1. Diffusion and its phenomena

Diffusion is a mass transport phenomenon that occurs through migration of atoms. In solids, it is a sequence of atomic jumps from one to another site of a crystal [5]. Both, the migration paths as the positions of atoms are restricted by the crystal lattice [1][7]. The mechanisms of diffusion are crucial for understanding the behaviour of solids, especially at elevated temperatures. They have either vacancy, interstitial or substitutive character [65]. In binary systems, there are various diffusion phenomena present – self-diffusion, foreign atom diffusion, interdiffusion and reaction diffusion. The interdiffusion occurs in response to a concentration gradient [66] (gradient in chemical potential). In binary systems consists of two atomic diffusion fluxes supported by concentration gradients.

Reactive diffusion is the diffusion-controlled growth of phase layers between two reacting materials through interdiffusion [62]. The reactive diffusion results in the continuous formation of solid compound layer at the interface by a chemical
transformations taking place after diffusion of the species. These intermetallic compounds (IMCs) are ordered alloys, with their structure of preferential position of atoms (i.e. Laves-phase) stable usually up to the melting point. However, some IMCs undergo order-disorder transitions, where arrangement of atoms gets randomised. Such transitions occur i.e. in Cu-Sn binary for $\eta'$ transforming into $\eta$ phase with temperature. The intermetallics form for certain stoichiometric compositions only. Many intermetallic-based materials are known for their extraordinary properties – like high hardness and wear resistance, chemical stability, magnetic and superconducting behaviour [61] or even colour [36]. The IMCs are also known for the less wanted aspects, like high brittleness or low fatigue and fracture toughness [72]. There is an IMC formation sequence, when the single phase consumes the reactive base elements. The growth of newly formed phase usually demonstrates linear rather than parabolic time dependence. It is commonly reasoned that the diffusivity of the first grown layer strongly overcomes the diffusivities of other phases. However, it was shown that the linear stage of intermetallic layer growth may also be caused by a relaxation rate of non-equilibrium vacancies [60]. The thickness of the new phase depends on the kinetic parameters of the system [62]. The vacancies and interstitials defects serve as the diffusion paths inside the crystals. The atoms move at much higher rates through the grain boundary (GB) regions or free surfaces. The grain boundary diffusion in metals is of 5 orders magnitude faster than bulk diffusion. The difference increases with decreasing temperature due to the smaller activation enthalpy of grain boundary. The interaction of non-equilibrium vacancies with their sources and sinks at GBs provides specific manifestation of the Kirkendall and Frenkel effects and is responsible for generation and relaxation of diffusion stresses [64].

The microelectronic circuits are built on thin films, where the diffusion paths vary to the bulk samples. Particularly when miniaturisation of integrated circuits is in focus, the GB diffusion plays a major role and the bulk diffusion is negligible [60][63]. The diffusion and in particular GB diffusion is important at macro scale for creep, recrystallizations or sintering [65], but is crucial at micro scale to allow for the rapid formation of interconnections.

2.2. Diffusion based bonding technologies

The diverse techniques to join materials together to form structures are mainly differentiated by the way of bringing free surfaces into an intimate contact: me-
chanical (like fastening with screws or rivets), adhesive (glues and epoxies) or metallurgical (like welding, brazing or soldering) – Tab. 2.1.

Tab. 2.1. – Summary of bonding technologies [41].

<table>
<thead>
<tr>
<th>Method</th>
<th>Micro-joining</th>
<th>Nano-joining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-state bonding</td>
<td>Anodic, Wafer, Diffusion, Friction stir welding</td>
<td>Diffusion bonding, Ultrasonic and Electron beam welding</td>
</tr>
<tr>
<td>Soldering/Brazing</td>
<td>Diffusion, Eutectic, Wave, Reflow, Flip chip bonding</td>
<td>Reflow, Resistance, Active Laser, Diffusion</td>
</tr>
<tr>
<td>Fusion Welding</td>
<td>Electron and Laser Beam, Resistance</td>
<td>Laser beam, Resistance</td>
</tr>
<tr>
<td>Adhesive bonding</td>
<td>Adhesive die attachment, Adhesive flip chip bonding</td>
<td>Adhesive bonding</td>
</tr>
</tbody>
</table>

The metallurgical bond is achieved by interfacial reaction between filler metal or solder with surfaces to be joint. It commonly requires heat and/or pressure to be applied. Aside from welding, there is no pre-melting of parent material, and only inserted filler material reacts in the liquid state. The brazing and soldering apply different filler materials processed at different temperatures. The typical solder has to melt below 450 °C, whereas the brazing filler should have much higher melting point [42]. These processes are based on solid-liquid interaction. In microelectronics assembly, the variations of soldering techniques have been applied to utilize so called die-attach or packaging process. The diffusion bonding is used to join same or dissimilar materials. It requires application of sufficient pressure and heat not exceeding the melting point of any involved materials over a longer period of time – solid-solid interaction. The diffusion process reorients surface atoms and allows for reaction at the interface resulting in adhesive and later cohesive joint between the components [1][43]. The benefits provided by the diffusion bonding together with handiness and industrial application of conventional soldering are brought together in a process called Transient Liquid Phase bonding. As any other typical metallurgical bonding, the TLP employs an interlayer of low melting point material, placed in-between the surfaces of materials to be joined [70]. The difference to those technologies stands up in the mechanism of the bond formation that does not proceed through solidification upon cooling. At bonding temperature, when the liquid phase of the filler is formed, the enhanced mass transport rates are observed. This interdiffusion of atoms over the liquid-solid interface is followed by isothermal solidification and homogenization still at that high temperature. Once these processes are complete, the resulting bond is able
to withstand operation at temperatures higher than the bonding temperature [44].

The TLP bonding is a registered trademark of Pratt & Whitney since 1972, however, the technique has been known and used before. More generally it is called an activated diffusion bonding, diffusion brazing or diffusion soldering, distinguishing upon materials and temperatures applied [43]. It is also referred to as solid-liquid interdiffusion or simply isothermal solidification. The most advanced TLP processes have been developed for aerospace industry, in particular Ni-superalloys. However, many other metal-metal and metal-ceramic combinations can be joined in that manner, i.e. Ti, Co or Al alloys and steels. Depending on the material system, the processes enables formation of “invisible joint” across interlayer of the filler material, with microstructure and properties identical or close to those of the base metal [45]. There are however few critical issues about TLP processes. The amount of the liquid phase formed plays an important role as the extensive diffusion of interlayer metal element into the base metal must occur. This depends on the mutual solubility of filler and the base metals, as well as the kinetics of the interdiffusion process [45]. Therefore, with the great potential of the TLP bonding, major obstacles are still given for its application in microelectronic assembly.

2.3. Transient Liquid Phase Bonding for microelectronics

Transient Liquid Phase Bonding has attracted significant research attention as a substitute for conventional Pb soldering. The method has been under research for packaging of power devices and for 3D integration [46]. The materials system reported are mainly Cu-filler binaries, but also Au-In and Ni-Sn [47], Au-Sn [48], Ag-Sn [49]. The Cu-filler systems were investigated for the isothermal solidification for over 20 years. The examples include combinations of Cu-Sn [44], Cu-BiIn, Cu-In, Cu-SnI [48]. For Cu-Sn system, the growth mechanism of the intermetallic compound (IMC) was investigated, establishing that IMC formation between liquid Sn and solid Cu, does not block further interdiffusion and transformation of Sn into IMCs [50]. To obtain a joint that could withstand higher re-melting temperatures, all present interlayer material has to be transformed into an IMC phase(s). However, for the low soldering temperature the kinetics of the reactive diffusion is very slow. It has been proven possible to form low heat resistance interconnect between Cu-Sn in the TLP process, followed by an additional annealing step [51]. The after-bonding annealing is known as a limitation for the TLP to be applied for packaging, since to achieve a full transformation of 5 µm Sn into
Cu₃Sn phase, the 16 h of annealing time at 280 °C is required [51]. Such intensive processing time is not suitable for industrial process, since a typical solder re-flow profile consists of the order of 200 s at temperatures just below the melting point of the alloy. Therefore the homogenisation time is seen as a major drawback for the use of TLP process as the alternative bonding technology for microelectronic processing [52].

Other studies demonstrated that the initial solid-state formation of IMC at the interface during the heating up phase limits the quality of the TLP bond between Cu-Sn. This leads to a formulation of critical interlayer thickness for successful pore-free bonding [44]. The critical thickness of the interlayer is limited by the mobility of species and should exceed the thickness consumed through the solid-state reaction. Otherwise, no liquid is formed at the processing temperature and the bonding cannot occur, which sets a minimal requirement on the interlayer thickness. Providing thicker interlayer, the subsequent isothermal solidification occurs by diffusion of the interlayer material into the base material [44].

Since currently there is still no obvious solution for the assembly for power electronics of the future, this aspect stands in the motivation of the current work. For this purpose the Cu-Sn system was chosen as the model system to study the possibilities of rapid formation of interconnects.

2.4. Cu and Sn alloys

Cu has a face-centre cubic lattice with the cell parameter of 3.615 Å and atomic weight of 63.5. Its density measures 8.96 g/cm³ [6]. Similarly to Ag and Au, its’ interatomic interactions are governed by half occupied s shell on top of filled d shell, meaning the Cu atomic bonds lack the covalent character. Cu is one of the four elements that have a colour different than grey or silver. The origin of its colour comes from the energy difference between the s and d orbitals in the range of orange light wavelength. With its electronic and crystal structures, Cu is highly conductive – both electrically with 60x10⁶ 1/(Ωm) and thermally with 401 W/(Km) at room temperature [7]. Surface energy of Cu per unit area is γ_{Cu} = 1.25 J/m² with a typical value of stacking fault energy of 80 mJ/m² [56]. Pure Cu melts at 1085 °C and forms number of alloys. The Cu alloys with Zn (brass) and Sn (bronze) are the most well-known and used materials. Pure Cu is mainly present in electrical products. The high conductivity of Cu makes it very attractive for microelectronics both as substrates, device metallization layers, as well as solder alloys constituents [9][10].
Sn is a main element in the currently used solder alloys in microelectronics. Sn melts at the temperature of about 231 °C for bulk, reduced to 176 °C for 11 nm particles [11]. The Sn exists in two crystallographic configurations, the metallic body cantered tetragonal (bct), so called β-Sn (density 7.29 g/cm³) and non-metallic, cubic, stable below 13.5 °C α-Sn (5.77 g/cm³) [12]. The transformation temperature can be lower or the transition may not occur at all when impurities are present in the material. The tetragonal form has lattice parameters of 5.83 and 3.18 Å and weights atomically 118.7. The density of liquid Sn is close 7 g/cm³[6][12]. Sn forms simple eutectic systems with Pb, Bi, Ga and Zn [54][55]. The technologically beneficial properties of the Sn-Pb alloys [54][55] made them the major packaging materials used for soldering in microelectronics assembly. With other metals the phase diagrams are rather complex, with low solubility of an element in Sn and many intermetallic phases. Cu is one of the materials with which the Sn forms highly complex phases over the composition change [13][14]. The Cu-Sn alloys are commonly known as bronzes (rich Cu) and solders (rich Sn). The system is characterized by a series of peritectic and eutectic reactions and shows several equilibrium intermetallic compounds, as well as the two terminal solid solutions (Fig. 2.1) [15][16].

The Cu-Sn eutectic composition is 99.3 wt.% Sn and 0.7 wt.% Cu 227 °C. The eutectic microstructure of Cu-Sn consists of β-Sn and the finely dispersed interme-

![Fig. 2.1 – Phase diagram of Cu-Sn [24].](image)
tallic compound – Cu₆Sn₅ (η phase). The η phase has a Sn concentration of around 60 wt.% and crystallizes in an ordered, hexagonal lattice. The number of Cu and Sn sites is equal. It is based on a modified close-packed (ABACABAC type) sequence. The Cu atoms fill the A location (octahedral interstitial sites) and the Sn atoms stay at B and C locations (hexagonal close packed sites). The composition is achieved with an additional Cu atom, located at the 1/10 of the tetrahedral interstitial sites in the hexagonal lattice [13][14][16]. The phase undergoes a secondary ordering into long period super-lattice η'-Cu₆Sn₅ around 186 °C. At 415 °C it undergoes a peritectic reaction and stays in equilibrium with the Sn-rich liquid and the ε-phase. The ε-Cu₃Sn, with 38 wt.% Sn, solidifies in orthorhombic crystallographic structure. The ε-phase exists from room temperature to 675 °C. The ε-Cu₃Sn has a long period, close packed structure (ABAB), based on the orthorhombic structure [13][17][24]. The ζ-Cu₁₀Sn₃ is a hexagonal superstructure [18]. The δ-phase (Cu₄₁Sn₁₄) with 32.5 wt.% Sn has a face centred cubic structure and is stable between 350 and 582 °C. The δ-phase undergoes an eutectoid reaction at 349 °C where it decomposes upon cooling to a two-phase microstructure of ε and (Cu). Another eutectoid reaction occurs at a temperature of 520 °C, where the high temperature γ-phase decomposes to δ and (Cu). At this temperature the Cu solid solution dissolve up to 15.8 wt.% Sn, but the solubility limit decreases to zero as room temperature is approached. The phases and their lattice parameters are listed in the Tab. 2.2.

The atomic arrangement and the reorganisation of atoms between Cu and Sn unit cell were studied extensively. The atoms on the closest packed crystallographic planes – fcc (111) and (001) hcp – arrange in the same hexagonal pattern, but a different plane arrangement (stacking faults) [13]. The Cu atoms are about 20% smaller than the ones of Sn. That means the Cu layers have a reasonable amount of space between atoms, when the lattice is close packed on the Sn layer and there are open channels along the C sites in the close packing [13]. The concentration of stacking faults increases with the quantity of a dissolved metal in the (Cu) distorting the crystalline structure. The thermodynamics of the material provide the fundamental information on solubility of phases, the driving forces for chemical reaction and for diffusion processes occurring for any metallurgical process in bulk or thin film geometries. The standard Gibbs free energy for pure Cu and Sn is listed in the Tab. 2.3 and for the Cu-Sn IMC in the Tab. 2.4. IMC formed during reactive interdiffusion of pure elements have lower values of the Gibbs energy of formation than the phases formed sequentially from already existing other. In the Cu-Sn thermodynamic assessment, more than one IMC exists – Cu₆Sn₅ aside of Cu₃Sn. The Cu₃Sn phase has a lower Gibbs free energy of for-
mation, meaning that thermodynamically speaking, it should decompose into a phase with a higher Gibbs energy of formation – Cu₆Sn₅ phase.

### Tab. 2.2. – Phases found in Cu-Sn phase diagram [6][15][24].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molar ratio of Sn</th>
<th>Crystal lattice</th>
<th>Lattice parameter, Å</th>
<th>Pearson symbol</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ-Cu₁₁Sn₁₁</td>
<td>0.21</td>
<td>cubic</td>
<td>17.96 17.96 17.96</td>
<td>cF416</td>
<td>Cu₁₁Sn₁₁</td>
</tr>
<tr>
<td>Ϟ-Cu₁₀Sn₃</td>
<td>0.23</td>
<td>hexagonal</td>
<td>7.31 7.31 7.87</td>
<td>hP26</td>
<td>ζ-AgZn</td>
</tr>
<tr>
<td>ε-Cu₃Sn</td>
<td>0.25</td>
<td>orthogonal</td>
<td>5.52 3.81 4.33</td>
<td>oC80</td>
<td>Cu₃Ti</td>
</tr>
<tr>
<td>η-Cu₆Sn₅</td>
<td>0.45</td>
<td>hexagonal</td>
<td>11.02 7.28 9.83</td>
<td>hP4</td>
<td>AsNi</td>
</tr>
</tbody>
</table>

However, it is known that the phase formation in Cu-Sn is governed kinetically, and that Cu reacts at room temperature spontaneously with Sn forming Cu₆Sn₅, and the Cu₃Sn phase forms only at temperatures above 60 °C [3][33][34]. The nucleation at room temperature requires much higher undercooling than at 60 °C, meaning Cu₃Sn nucleates, but it cannot compete against Cu₆Sn₅ with the growth rates. The later formation of Cu₃Sn happens at the expense of Cu₆Sn₅ [20].

### Tab. 2.3. – Standard Gibbs free energy \(^\circ G^T\) for pure elements [19][20].

<table>
<thead>
<tr>
<th>T, °C</th>
<th>25</th>
<th>150</th>
<th>180</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^\circ G^T_{Cu}) [kJ/mol]</td>
<td>-9.9</td>
<td>-14.6</td>
<td>-15.9</td>
<td>-16.7</td>
</tr>
<tr>
<td>(^\circ G^T_{Sn}) [kJ/mol]</td>
<td>-15.25</td>
<td>-22.3</td>
<td>-24.15</td>
<td>-25.4</td>
</tr>
</tbody>
</table>
The literature states the noble metals diffuse in β-Sn through an interstitial mechanism. Cu diffuses exceptionally quickly in the interstitial sites of Sn, In and Pb (group IV of the periodic table) [20][21]. It has been observed that mobility of Cu in Sn is high enough to form IMC already at the room temperature. However, it decreases strongly with the increasing concentration in the solvent. The diffusivity of Cu is claimed to happen along the a- and c-axes of β-Sn and is in the order of $0.5 \times 10^{-8}$ and $2 \times 10^{-6}$ cm$^2$/s, respectively [20]. On the other hand, Sn diffuses through Cu by much slower substitution mechanism. There is however still an open scientific discussion, which element is a dominant diffusion species in the solid-state IMC formation. At room temperature molar volumes of Cu, Sn, Cu$_3$Sn and Cu$_6$Sn$_5$ are 7.1, 16.3, 27.3 and 118.0 cm$^3$/mol, respectively [26]. Due to Cu-Sn IMC formation, certain volume shrinkage cannot be compensated and results in the existence of Kirkendall voids$^2$ in direct proximity or at the interface of the Cu$_3$Sn phase [17][20][26]. The literature explains this behaviour, with Cu being the main diffusion species, although the Sn diffusion must occur as well but at the lower rates. Diffusion controlled solid-state reaction are phase transitions in a concentration gradient (interdiffusion). The vacancy fluxes are the result of different mobilities of the diffusing species. The molecular dynamic simulations provide information that the diffusivity of Cu is a dominant diffusion species in the Cu$_3$Sn compound. The diffusion coefficient is 17 times higher at room temperatures and 7 times higher at 150 °C than for Sn. This large difference is believed to be the main reason for Kirkendall void formation [57].

---

$^2$ The Kirkendall effect is commonly accompanied by the Frenkel effect, the void formation in the diffusion zone. The Frenkel effect is often referred to as Kirkendall voiding, although these effects are competitive: vacancies annihilating at the dislocation kinks cause the Kirkendall shift, cannot be used for Kirkendall voiding, and vice versa

Tab. 2.4. · Summary of energy of Cu·Sn IMCs formation

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ethalpy of formation, kJ/mol</th>
<th>T, °C</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{41}$Sn$</em>{11}$</td>
<td>-5.7, -5.45</td>
<td>450</td>
<td>[22]</td>
</tr>
<tr>
<td>Cu$_{3}$Sn</td>
<td>-8.2, -7.81, -7.82, -8.36</td>
<td>450</td>
<td>[22], [23], [25]</td>
</tr>
<tr>
<td>Cu$<em>{6}$Sn$</em>{5}$</td>
<td>-6.1, -7.03</td>
<td>0</td>
<td>[22], [25]</td>
</tr>
</tbody>
</table>
The interfacial reaction between Cu and Sn occurs, when the metallurgical contact is assured and the dissolution of Cu in Sn starts. Initially, the dissolution rate is very high, thus high concentration of solute elements are locally realised. The intermetallic compounds form to govern the local equilibrium. The IMC layers ranges from a very high concentration of Sn on the solder side to a high concentration of Cu on the base material side. The growth of these phases are reported to follow the Arrhenius relationship, with the activation energy for Cu₆Sn₅ being around 0.5 eV and for Cu₃Sn around 1.15 eV [27][31]. This means that the growth of Cu₆Sn₅ is quicker than Cu₃Sn for bulk. The growth kinetics of the intermetallic phases Cu₆Sn₅ and Cu₃Sn in the films with fine polycrystalline structure is experimentally claimed to be several times higher due to the grain boundary diffusion, in respect to the bulk samples [26][28]. By using X-ray diffraction, it was detected in a Cu-Sn thin film diffusion couple on quartz that Cu reacts with Sn at room temperature to form the Cu₆Sn₅, even after the period of one year [39]. However, Cu₆Sn₅ grows at the higher rate at temperatures above 136 °C. The absence of Cu₃Sn nucleation is argued with high activation energy of formation (119 KJ/mol). The observed Cu₃Sn comes from transformation of Cu₆Sn₅ [4].

The reactive diffusion leading to phase formation in thin films occurs sequentially, despite the fact that the equilibrium phase diagram describes co-existence of several stable intermediate phases. The other compound grows only after the reactive materials have been consumed and the initial phase has no more material for growth. Such sequential mechanism is originated in the maximum diffusivity of the compound that is grown first. It creates a state of the diffusive interaction, where the growth of the phases with lower diffusivities is even more restricted than if they would form alone. This interaction between neighbouring phases may suppress the formation of the critical nuclei or the other phases exist and grow, but too slowly making them undetectable [30].

In diffusion controlled growth the concentration at the interface is assumed to have an equilibrium value. However, in the interface reaction controlled growth, the concentrations at the interface are assumed to be non-equilibrium. The thicker compound layer slows down the growth rate of the compound. At such low rates none of the compound layers can be consumed by the growth of the other and they co-exist (and grow) at the same time (diffusion controlled growth). If the growth rate is independent of the layer thickness, a sequential growth can be seen (interfacial reaction controlled growth). However, this state is limited to a certain thickness threshold, where the mass transport across the layer will limit its rate. It will then be described further by diffusion controlled growth (I Ficks
Law) or its time dependence will transfer from linear to parabolic [Sauders 90, Booth 1977].

The above mentioned processes define Cu-Sn behaviour during bond formulation. The procedure suffers from a very fundamental rate limiting step – the kinetics of the interfacial bulk reaction in the solid-state. The current technological solutions manage to by-pass the higher (or too high) processing temperature of the components by use of the post-process annealing at lower temperature, however an overall quick processing is not achieved. The control of diffusion in Cu-Sn system, would allow for the rapid intermetallic formation into the current microelectronic assembly scheme.

2.5. Control of the solid-solid and solid-liquid diffusion

Accelerating the bond formation in the TLP process means the acceleration of the reaction kinetics. In order to reduce the time required for atomistic diffusion, the reduction in diffusion distances or the increase in quick diffusion paths are required. In joining, the presence of liquid phase discards the issue of quick diffusion paths, like grain boundaries on the solder side. The reduction of the process time is considered to be realized through minimisation of the effective diffusion distance through the amount of the filler alloy or its form. It has been reported in the literature, that reducing the relevant diffusion distance during the TLP bonding process, accelerates kinetics of the bond formation [58]. Introducing the filler material in the design of the powder mixture (filler metal and base material) has been proposed as the solution for speeding up the TLP process (referred to as TLP sintering). The example of the thick TLP joints on stainless steel was demonstrated with the use of the filler consisting of Ni-P coated Ni-Cr alloy powders and stainless steel powders [59]. It was found that time required for isothermal solidification to join Ni-based superalloy with heterogeneous interlayer composed of mixtures of base powders and filler, could be reduced by two orders of magnitude as compared to joints with homogenous interlayer consisting of pure filler [58]. It clearly demonstrates the impact of reducing the relative thickness of the interlayer onto the kinetics of the joining reaction. However, the mentioned material system possesses much slower reaction kinetics, than Cu-Sn and the phenomenon of solid-state interdiffusion consuming the filler prior to bonding was not reported.
Chapter 3. Goals and objectives

As synthetically summarised in the previous chapter, the control of materials interaction at reduced dimension offers many opportunities for industrial applications. In particular, within the development of new joining processes, i.e the microelectronic assembly the possibility to use “nano”-systems to shorten relevant diffusion distance and herewith the processing time. The overall objective of this work is to make the progress in this direction by exploring ways to control mass transport occurring between Cu-Sn at reduced dimension that could be utilised for rapid formation of interconnects. In this framework, two methodological approaches were defined to assess solid-solid and solid-liquid stages of isothermal interdiffusion.

The specific goals of this work are:

(i) understanding of the limitations provided by the Cu-Sn systems for the rapid microelectronic assembly through
   - description diffusion kinetics in Cu-Sn isothermal solidification
   - analysis of heating rate effect on the reaction rate on the liquid-solid bulk interdiffusion in Cu-Sn system
   - explanation of the joint formation mechanism involving heating rate effect
   - design and assembly of the rapid thermal annealing furnace required to preclude the main part of the current study;

(ii) hindering of the solid-state diffusion, and herewith the study of liquid-solid interactions through incorporation of a temporary diffusion barrier layer in powder mix compacts:
   - characterisation of reaction kinetics in bulk with applied diffusion barrier in form of Sacrificial Passivation
   - design and formulation of passivated metallic particle
   - investigation of thermal stabilisation effect of passivation on the Cu and Ag powders
   - incorporation of sacrificially passivated powders to shorten the diffusion distance and allow for rapid IMC formation and formulation of robust and reliable particle synthesis procedure
- evaluation of the extend of solid-state reaction in sintered powder mix compacts;

(iii) an exploitation of solid-state reaction and diffusion through:

- kinetic study of solid-state diffusion for rapid intermetallic formation with incorporation of nano-multilayer methodology with:
  - identification of dominating diffusion species during reaction diffusion in Cu-Sn thin films and the comparison to the macro-scale behaviour,
- thermodynamic description of thermally driven redistribution of IMC phases through:
  - characterisation of scale effects in the initial IMC formation at room temperature (RT) of the Cu-Sn nano-multilayers and description of critical length scale conditions for the occurrence of nano-effects,
  - theoretical assessment of identified IMC in nano-multilayers upon heating and comparison to macro-scale behaviour

By control of the solid-state diffusion at the nano-scale, as elaborated within the framework of this study, the joining process enables upon optimisation the rapid formation of interconnects for the microelectronic assembly. The fundamental knowledge gained throughout this study is to be exemplary applied to an application-oriented joining process.

Therefore, the terminal aim of this work is to formulate a methodology to control reactive diffusion in Cu-Sn (and reference systems) and achieve a rapid and full transformation of the constituents into an intermetallic compound. However, since this work aims at improving the understanding of the diffusion steering in reactive interdiffusion rather than maximizing the performance of the joints, the study concentrates on the phase formation and effect related to each of the approaches chosen, rather the characterisation and optimisation of the joint formation.
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[69]. F. Geng, J. Qu, Materials Letters (2012), 73, 92, „Calculating the diffusivity of Cu and Sn in Cu₃Sn intermetallic by molecular dynamics simulations”


Part 2. Experimental design

The different aspects of the current study with focus on control of solid-state diffusion in Cu-Sn were investigated and analysed. The know-how of control gain over the interface interaction was achieved through exploitation of pure solid-state diffusion and temporary inhibition of the solid-state interaction during processing.

Chapter 4. Methodology

The main objective of this work is to achieve the control over diffusion that would allow to formulate the rapid interconnect procedure. As such, investigation of different aspects of diffusion control focuses on Sn interaction, defined as filler material, with Cu (or in special cases Ag or Au) as base material, taking at the same time into consideration the procedural parameters, like its size and metallurgical reactions.

The experimental work was divided into three parts:

(i) study of rapid heating during solid-liquid joint formation
(ii) full but temporary inhibition of the solid-state interaction in powder mix compacts using Sacrificial Passivation, a specifically designed polymeric coating
(iii) exploitation of pure solid-state diffusion by nano-architecturing of the filler material with the nano-multilayer approach applied

Each of these approaches was demonstrated through particular experimental design. Since this work aims at improving the understanding of the diffusion steering in reactive interdiffusion rather than maximizing the performance of the joints, the study focused on the phase formation and effect related to each of the approaches chosen.
4.1. Materials

The oxygen-free, high conductivity Cu (99.99%) was obtained from Alfa Aesar in a wire and a rod form. The wire was used to prepare the target for electron beam depositions. The rod of 10 mm diameter was sliced into 2 mm thick coupons. The coupons were used for joining and coating experiments; they were final polished, dunk in 5% HCl/ethanol solution and rinsed with distillate water prior experimental trials.

The Sn (99.9%) was obtained from Goodfellow in the form of a micron-size powder, wire and foil of 38 μm. The powder was used for producing powder compacts. The wire was used for electron beam evaporation as the target material upon remelting. The foil was used in joining experiments. Prior to assembly it was cleaned in 1:6:6 mixtures of 35%H2O2:25%NH3:H2O to remove the native oxide.

The Si wafers used for the support of deposited films were purchased from Si-Mat. The wafers were coated with a diffusion barrier coating of SiNx w/o TaN to assure the lack of chemical interaction between the substrate and the deposited films.

The materials for Sacrificial Passivation were chosen upon the feasibility study. For the synthesis of Cu particles – two organic molecules were selected polyvinylpyrrolidone (PVP) (Sigma, MW 30,000) and sodium dodecyl sulphate (SDS) (Fluka, Biochemical grade, > 99 %). For the synthesis of Ag particles – three organic molecules were selected polyvinylpyrrolidone (PVP) (Sigma, MW 30,000), poly(vinyl alcohol) (PVA) (Sigma, MW 31,000-50,000, 99 % hydrolysed) and sodium dodecyl sulphate (SDS) (Fluka, Biochemical grade, > 99 %). The details respective this part of the study is described together with the reactants and procedures used for chemical synthesis in the later section.

4.2. Experimental details

Based on the approach used, the specific experimental formulation of the samples was defined and applied. For the conventional solid-liquid joining and solid-solid diffusion couple experiments, sandwich type samples were applied. For tempo-
rary blocking of the solid-solid interaction the powder approach was chosen. For rapid solid-solid interaction the nano-multilayer geometry was used.

4.2.1. Rapid heating in conventional joining

The study is supported by the analysis of the joining process for microelectronic assembly. The limitation of solid state diffusion during a conventional bonding process in standard sandwich geometry was investigated. The heating rate effect strategy was demonstrated on the Cu-Sn couples to reconstruct the typical bonding geometry in the low melting point configurations. The procedural parameter of focus – heating rate – as suggested in the literature to bear the main potential for the process was analysed. And a customised laboratory scale furnace has been designed and assembled, so called Rapid Thermal Annealing (RTA) with the heating rates stable reaching 350 °C/min.

The Rapid Thermal Anneal (RTA) furnace was designed to provide for rapid, exact heating of small samples under an inert or forming gas environment. The distinct feature is its extremely high heating and cooling rates (~ 350 K/min) enabled by the use of high intensity infrared lamps as the heat source. The heating characteristic is given in the Result Chapter 6.2. The furnace was designed and custom assembled in-house. The heating is achieved via two 1000 W infrared lamps aimed at a SiC susceptor. This susceptor absorbs the electromagnetic radiation of the lamps converting it into heat and transfers it to the sample fixed upon it. Since all other materials within the furnace are transparent or reflecting to the lamps radiation, only the mass of the susceptor and sample are heated, thereby providing extremely high and controllable heating. The exact specification is given in the Appendix I.

The procedural parameters for joining trials were – set point, dwell time and heating rate. The set point differed upon the experiment from 250 to 350 °C, chosen upon technical requirements of the process. Dwell time varied from 30 s to 10 min, and the heating rate from 20 to 350 °C/min. The sample arrangement in the holder and in the furnace is given in the Fig. 4.1.
The Fig. 4.1 shows the scheme of the sample holder in the RTA glass tube.

The Fig. 4.2 shows the read-out of thermal profiles with different heating rates and dwell times reaching the set point of 250 °C.

Fig. 4.2 – Real heating profiles applied for the Cu/Sn/Cu in sandwich joint geometry. The 20/10/250 indicated heating rate (°C/min)/dwell time (min)/set point (°C).
4.2.2. Sacrificial Passivation approach to diffusion couples and powder mix compacts

The inhibition of solid-state interaction between components using Sacrificial Passivation as a temporary kinetic barrier was introduced in form of the thin polymeric coating. The term Sacrificial Passivation describes an organic coating passivating against undesirable reactions until it is “sacrificed” to allow the reaction to proceed. The term was initially introduced with a research of Prof. J. Janczak-Rusch, at Empa Switzerland in 2008 [8] in the co-operation with the current study. The coating was applied between Cu and Sn, and compared against another couple of Ag-Sn. The approach involved study of passivated diffusion couples (macro-scale) and interaction between fine particles in powder mix compact. The incorporation of the coating in diffusion couple occurred with spin coating, for the powders the chemical methods were chosen.

Passivated diffusion couples

The spin coating was used to obtain thin planar films of Sacrificial Passivation for the feasibility studies. The technique is a simply and commonly used in microelectronics process for the deposition of ultra-thin (< 200 nm) and uniform coatings from the solution. The viscous forces and volatility of the solvent dominate the process that involves spreading a polymer solution over a substrate and rotating at the constant speed until the solvent evaporates and the film dries out. The coating layer thickness is a function of the concentration of the polymer solution and the rotation speed [6][7]. Fig. 4.3 illustrates the main steps of the process.

Fig. 4.3 – Illustration of standard spin coating process – application from solution, spreading of the solution through centrifugal force forming a thin wet film, evaporation of the solvent during rotation.
The PVA for passivation study was dissolved in distilled water of 90 °C upon stirring. A pre-filtration step was applied to assure clearance of the solution. The organic thin layers were spin coated on Si wafers with an ATM spin coater with a pre-rotation of 500 rpm to uniformly distribute the volume of the solution over the surface. The coating rates and times differed between 2000 and 6000 rpm for 30-60 s.

The fabricated sandwich type samples Cu/coating/Sn and Ag/coating/Sn were used as passivated diffusion couple. This study was performed in laboratory scale vacuum furnace (custom made TU Eindhoven). The initial parameter assessment was performed to understand and adjust the heating profile in order to form a metallurgical bond with the Sacrificial Passivation coating in the pure solid state interaction. This resulted in the thermal profile allowing for (at least) partial interfacial reaction between the passivated components. The passivated Ag/Sn and Cu/Sn diffusion couples were heated according thermal profile 60 °C/h, 1 h @160 °C, 60 °C/h, 30 h @200 °C, -600 °C/h under 5 kg weight.

Passivated Particles

The chemical synthesis was used to sacrificially passivate metal particles and prevent the solid-state interdiffusion in a powder compact. This organic cap was produced in-situ with the particles of base metal. These encapsulated particles were mixed with Sn powders to produce powder compacts. The capping agents used to encapsulate the particles during their formation were chosen upon their decomposition temperatures T_d that corresponded with the melting point of Sn. The final selection of synthesis parameters and their effects was a vital part of this part for the current work. The experimental setup is shown in Fig. 4.4.
The design of experiments (DOE) derived from the Taguchi methods [9], was implemented to optimise the experimental conditions of the reduction synthesis, in order to obtain a desired characteristic of the organic encapsulation over Ag and Cu particles. The Ag-Sn was chosen as the control system against Cu-Sn. Considered responses were the temperature and mass of decomposition of the organic encapsulation. Reducing agent, organic molecule, addition rate and addition ratio were chosen as the main parameters based on preliminary experiments for the orthogonal array (OA). Additionally a matrix model describing the behaviour of the synthesis system was elaborated taking into account the effects of each considered parameter and their interactions.

Synthesis of passivated Ag particles
Procedural factors affecting the decomposition temperature of Sacrificial Passivation were defined as: (i) synthesis route, (ii) organic molecule, (iii) molar ratio of the precursor metal salt to organic molecule and (iv) addition rate of the metal
salt to the reaction mixture and their effect on the thermal response of the Sacrificial Passivation [11]. Three synthesis routes and three types of organic molecules were taken into account. The molar ration varied between 0.5, 1.5, or 5 times the molar content of the metal salt, the addition rate varied 0.5, 5 and 50 ml/min. The reaction scheme:

\[ \text{Ag}^+ + \text{Capping Agent} \xrightarrow{\text{Reducing Agent, Temperature}} \text{Ag} \cdot \text{Capped} \]

Varying the parameters of the synthesis has tuned the formation of particles and influenced thermal response of the passivation layer. The details are listed in the Tab. 4.1.

Tab. 4.1. – Description of the procedural factors of the chemical synthesis used to study passivation behaviour of the encapsulation on Ag particles

<table>
<thead>
<tr>
<th>(i) Synthesis route</th>
<th>Route (a), ethylene glycol (EG)</th>
<th>Route (b), ascorbic acid</th>
<th>Route (c), glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml of EG was heated to 160 °C for one hour under constant stirring. From separate dropping funnels, solutions of AgNO3 (0.0015 mol, 0.25 M EG) and the organic molecule (in 6 ml EG) were added to the system (reaction mixture turns light tan), reacted for one hour under constant stirring and allowed to cool to room temperature.</td>
<td>The organic molecule was added to 6 ml of EG and heated to 160 °C for one hour under constant stirring. From separate dropping funnels, solutions of AgNO3 (0.0015 mol, 0.25 M EG) and ascorbic acid (0.003 mol, 0.5 M aq) were added (reaction mixture turns light brown), reacted for one hour under constant stirring and allowed to cool to room temperature.</td>
<td>The organic molecule, glucose (0.04 mol) and sodium hydroxide (0.28 mol) were added to 60 ml of water and brought to 60 °C under constant stirring. A solution of AgNO3 (0.005 mol, 0.25 M aq) was added (reaction mixture turns deep purple), reacted for 10 minutes under constant stirring and allowed to cool to room temperature.</td>
<td></td>
</tr>
</tbody>
</table>

(ii) Organic molecules

The three organic molecules selected were polyvinylpyrrolidone (PVP) (Sigma, MW 30,000), poly(vinyl alcohol) (PVA) (Sigma, MW 31,000-50,000, 99 % hydrolyzed) and sodium dodecyl sulfate (SDS) (Fluka, Biochemical grade, > 99 %).

(iii) Molar ratio of precursor metal salt to organic molecule

The amount of organic used served as the next procedural factor with the three levels of 0.5, 1.5, or 5 times the molar content of AgNO3.

(iv) Addition rate of the metal salt to the reaction mixture

The final factor of salt solution addition rate was varied at the three levels of 0.5, 5 and 50 ml/ min.
Following synthesis, the particles were isolated from solution through a repeti-
tious procedure of washing and centrifugation. Each reaction solution was dilut-
ed with water (25 times by volume) and centrifuged (4000 rpm for 20 minutes).
The supernatant was then disposed and acetone used for redispersion and
subsequent centrifugation. This was repeated four times. Following the final cen-
trifugation, the isolated particles were dispersed in ethanol and the solution
dried at 50 °C under vacuum for 24 hours to produce a powder for subsequent
characterization.

Each factor was explored over three levels. All these factors would generate 81
trials needed to observe all possible combinations. The reduction of trials was
possible through an application of experimental design. The experimental design
and data analysis was provided by means of a Latin Square orthogonal array of
nine repetitions (L9) that could position four and three-level factors reducing the
number of required trials. Tab. 4.2 contains the experimental factorial with the
specific levels used in this study according to Taguchi DOE and the employed
procedural factors in this study are shown in Tab. 4.3. After realizing the exper-
iments with the parameters in the corresponding levels, the choice for the level of
each factor can be determined to optimise the responses. The study of interaction
between the factors was additionally performed.

Tab. 4.2. – Taguchi design of experiments based on L9 orthogonal array for the Ag parti-
cles synthesis

<table>
<thead>
<tr>
<th>Trail</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>i</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
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<td>4</td>
<td>2</td>
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<td>2</td>
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<tr>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>
Synthesis of passivated Cu particles

For the design of experiments (DOE) for the synthesis of encapsulated Cu particles the Taguchi Method was employed. Based on the Ag experience, the determination of the investigational parameters was complemented with investigation of interaction between factors. A Latin Square orthogonal array of eight repetitions (L8) has positioned three, two-level factor columns as well as a column for the observation of interaction. To fully observe the presence of an interaction, all experimental trials had to be performed. The L8 orthogonal array employed is presented in Tab. 4.4 with factors i-iii at levels 1 and 2.

Tab. 4.3. – Corresponding L9 array of experiments assigned for the Ag particles synthesis

<table>
<thead>
<tr>
<th>sample</th>
<th>Factor</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>route</td>
<td>organic</td>
<td>ratio</td>
<td>rate (ml/min)</td>
</tr>
<tr>
<td>1</td>
<td>a</td>
<td>PVP</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>a</td>
<td>PVA</td>
<td>1.5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>SDS</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>PVP</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>b</td>
<td>PVA</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>b</td>
<td>SDS</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>c</td>
<td>PVP</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>c</td>
<td>PVA</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>9</td>
<td>c</td>
<td>SDS</td>
<td>1.5</td>
<td>50</td>
</tr>
</tbody>
</table>

Tab. 4.4. – Latin L8 orthogonal array based on Taguchi method for Cu experiments with interaction analysis

<table>
<thead>
<tr>
<th>sample</th>
<th>factor</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>2</td>
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<td>4</td>
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<td>8</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
The three procedural factors chosen for investigation of their effect on the caps decomposition temperature and relative amount: (i) organic capping agent, (ii) molar ratio of the precursor metal salt and organic molecule, and (iii) addition rate of the metal salt to the reaction solution. The ethylene glycol based synthesis was performed with each of organic molecules added to 10 mL of anhydrous ethylene glycol (EG) and heated to 140 °C under constant stirring for one hour. From separate dropping funnels, solutions of CuSO₄ (0.15 M, 10 mL) in EG and aqueous ascorbic acid (0.30 M, 10 mL) were added to the system and reacted under constant stirring for 1 h. The reaction scheme:

\[
\text{Cu}^{+2} + \text{Capping Agent} \xrightarrow{\text{Ascorbic Acid} \, 140 \, ^\circ\text{C}} \text{Cu - Capped}
\]

Upon stirring time, a small amount of ascorbic acid was added to prevent oxidation. The temperature was changed to 80 °C and the system was aged for one hour and allowed to cool down. Following synthesis, the particles were isolated from solution through a repetitious procedure of washing and centrifugation. The sample was diluted with 300 mL of ethanol and centrifuged (4000 rpm, 20 minutes). The supernatant was then disposed and the particles were re-dispersed in ethanol for subsequent centrifugations. This was repeated four times. Following the final centrifugation, the isolated particles were dispersed in ethanol and the solution dried at 50 °C under vacuum for 24 hours to produce a powder for subsequent characterization.

Tab. 4.5. – Description of the procedural factors of the chemical synthesis used for encapsulation on Cu particles

<table>
<thead>
<tr>
<th>(i) Organic molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>The two organic molecules selected were polyvinylpyrrolidone (PVP) (Sigma, MW 30,000) and sodium dodecyl sulfate (SDS) (Fluka, Biochemical grade, &gt; 99 %)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(ii) Molar ratio of precursor metal salt to organic molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>The amount of organic used served as a procedural factor with the levels 0.5 or 1.5 times the molar content of CuSO₄.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(iii) Addition rate of the metal salt to the reaction mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>The final procedural factor of salt solution addition rate was varied at the two levels of 5 and 50 ml/ min</td>
</tr>
</tbody>
</table>
The assigned levels are listed in Tab. 4.6. An interaction study was also conducted. An interaction describes the influence of one factor on another – molar ratio and the addition rate of the salt, resulting in the variation of the optimal experimental conditions for $T_d$ and M%. Molar ratio of the metal salt to the polymer and the addition rate of the salt were monitored in such a way as to identify the presence of an interaction between these two factors.

Tab. 4.6. – Corresponding L8 array of experiments assigned for Cu experiments with interaction analysis

<table>
<thead>
<tr>
<th>sample</th>
<th>organic</th>
<th>Factor ratio</th>
<th>rate (ml/min)</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVP</td>
<td>0.5</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>SDS</td>
<td>0.5</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>PVP</td>
<td>0.5</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>SDS</td>
<td>0.5</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>PVP</td>
<td>5</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>SDS</td>
<td>5</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>PVP</td>
<td>5</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>SDS</td>
<td>5</td>
<td>50</td>
<td>1</td>
</tr>
</tbody>
</table>

The reduction synthesis allowed stabilisation of fine powders (100-300 nm particles), but required the formulation and understanding of the synthesis procedures and the products thereof.

4.2.3. Nano-architecturing of multi-layer system

The architecturing of nano-multilayers to exploit phase transformations in pure solid-state interactions was demonstrated on Cu-Sn system with the main procedural parameter being a thickness of the Cu/Sn bi-layer leading to different Cu-Sn composition. The observations were enriched through application of a diffusion barrier layer in-between the Cu and Sn nano-layers (Appendix IV). The thickness models were defined and characterisation of the out comings is given.

In respect of exploitation of solid-state diffusion by nano-architecturing, the physical deposition methods were used. The physical vapour deposition (PVD) techniques are commonly used methods to construct the material film in the controlled thickness range, typically in sub-micron region [2][3]. The film is created
through the condensation of atoms (or ions) on the surface of substrate. The vapour phase of the coating material is generated through application of heat (via different sources) over the surface of deposited material causing evaporation or by argon ion bombardment of that surface causing sputtering. Such produced atoms (or ions) are deposited over the substrate [2][3][4][14].

All metallic films were deposited on a typical semiconductor wafer Si/SiNx (w/o TaN) with its role, limited to a physical support. The nitride coatings were used to assure lack of chemical interaction between reactive Cu/Sn layers and the wafer. The polycrystalline thin films (bi-layers and nano-multilayers) of Cu/Sn were prepared by means of physical vapour deposition without breaking vacuum and analysed using GI-XRD, RBS, and microscopy with EDX. Additionally, AES and XPS were used to support the analysis of the results.

Fig. 4.5 – Sketch of the multilayer geometry, with alternating layers of Cu and Sn.

The optimisation of deposition conditions was performed. Pure Cu, Sn, and Cu/Sn alternating layers (multilayers – Fig. 4.1) were prepared by means of e-beam evaporation at the Univex 500 evaporator available at FIRST, ETH Zürich. The evaporation happened in the evacuated chamber with a base pressure of 2x10⁻⁷ mbar under constant rotation of the substrate. The Cu and Sn were deposited at the rates of 3.2 Å/s and 2.4 Å/s respectively and were monitored with a quartz crystal rate mirror. All deposited Cu/Sn coatings incorporating W were dc magnetron sputtered from single metal targets at Paul Scherrer Institute, Laboratory for Developments and Methods, Villigen in the in-house assembled device. The films were sputtered at 100 W in high vacuum (base pressure below 9x10⁻⁷ mbar) with Ar mass flow of 5 sccm.

1 The scope of the current study did not involve the evaluation of electronic properties at any stage.
Chapter 5. Characterization techniques and measurement details

The samples from the diffusion couple experiments and the joining experiments were investigated by means of scanning electron microscopy (SEM) and characterised for the chemical composition with energy-dispersive X-ray spectroscopy (EDX). The effect of Sacrificial Passivation was studied with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology was observed by means of transmission electron microscopy (TEM) and chemical composition by standard powder diffraction (XRD). The thickness of spin coated organic thin layers was verified with an ellipsometer. The polycrystalline thin films (and nano-multilayers) were analysed using X-ray diffraction (in grazing incident geometry (GI-XRD), Rutherford backscattered spectroscopy (RBS), and microscopy SEM/EDX and TEM/EDS. The roughness was evaluated by atomic force microscopy (AFM). Additionally, auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to support the analysis of the results.

5.1. X-ray diffraction

To study the phase transition and growth of intermetallic compounds in thin films and nano-multilayers, as well as to identify the products of the chemical synthesis the X-ray diffraction techniques were used. The X-ray diffraction (XRD) is a powerful and most widely used technique to identify and characterize the crystalline phases and measure their structural properties. It offers a possibility of non-destructive, in-situ quantitative measurements for bulk materials as well as in thin films of minimum 10 nm [15].

The precision of the method comes from the Bragg diffraction that occurs when X-ray radiation of specific wavelength interferes on the successive crystallographic planes of the crystal lattice of the sample in accordance to Bragg’s law:

$$\lambda = n \cdot 2d \sin(\theta)$$

where $\lambda$ – wavelength, $n$ – order, $d$ – interplanar distance, $\theta$ – scattering angle.
Strong intensities known as Bragg peaks are obtained in the diffraction pattern when scattered waves satisfy the Bragg condition.

For the thin films few diffraction geometries are used, including grazing incidence XRD (GI-XRD). In GI-XRD, the X-ray probing depth is greatly reduced and the surface sensitivity down to 5 nm is possible (depending on the incident angle) with a standard X-ray source [15][17].

Phase identification in multilayers was performed with X-ray diffraction in grazing incident geometry using a PANalytical X’Pert PRO diffractometer at Laboratory for Solid State Chemistry and Catalysis, Empa Dübendorf, upon the preliminary analysis at CSEM Neuchatel. The diffractometer was equipped with a high temperature chamber. The data were measured in theta-2theta geometry, where the theta is an incident angle between the incoming beam and the sample and 2-theta an angle between the incident beam and the detector (Fig. 5.1). The angle of the incident beam was fixed at 3°. The CuKα radiation was used (Radiation: Cu-Kα1/2 (λα1=1.5406 Å; λα2=1.5444 Å). The in-situ heating experiments were run at constant heating from room temperature up to 450 °C under Ar/N₂ atmosphere, with a measurement every 10 °C. The data were analysed and compared the diffraction data base datasets X’pert pro and ICSD Karlsruhe database. The results were visualized in a two-dimensional (2D) plots by an appropriate software like ORIGIN™ and MAUD. The width of the reflection is usually inverse proportional to the grain size (in a direction perpendicular to the surface), provided other causes are neglected [30]. Rough stress estimation from the measured lattice strain was calculated with:

$$\sigma = -\varepsilon \cdot \frac{E}{2\vartheta}$$

where \(\sigma\) – lattice stress, \(\varepsilon\) – out-of-plane strain, \(E\) – elastic modulus, \(\vartheta\) – Poisson’s ratio.

For analysis of the powder synthesis, the conventional Bragg-Brentano geometry was used. These experiments were run on the Siemens/Bruker D5000 diffractometer available at the Laboratory for Nano-scale Materials Science at Empa Dübendorf using only CuKα radiation.
Due to nature of the Cu/Sn interactions (high roughness of the interfaces and strong interdiffusion between the components), the X-ray reflectivity (XRR), a standard technique for analysis of the nano-multilayers, could not be applied [12][13].

5.2. Ellipsometry

A thickness of planar thin organic films of the Sacrificial Passivation was evaluated with variable angle spectroscopic ellipsometer VASE M-2000FTM, available at the Laboratory for Surface Science and Technology, Department of Materials, ETH Zürich. The ellipsometry is a simple and non-destructive method used to characterise the material in terms of its optical constant, film thicknesses, surface and interfacial roughness [19]. The method is used to measure change of polarization of the light that is reflected from the surface. The light beam incoming on the surface of the sample is emitted from a light source and polarized by a polarizer. Upon reflection it goes through a polarizer (analyser) and falls into the detector (Fig. 5.2 (a)). The change of the polarization of the light beam is tracked back to change of refractive index of the layer in respect to the thickness [16] [20]. The thickness is determined by the fitted model based on Fresnel equations:

$$\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta}$$

where: $\rho$ – complex reflectance ratio, $r_p$, $r_s$ – Fresnel reflection coefficients for polarized light, $\psi$ – amplitude, $\Delta$ – phase difference.
The results on uniformity and the thickness of the coatings obtained from the ellipsometry measurements were used to determine the dependence of the parameters used for the spin coating to the existing thickness of the coated sample.

5.3. Thermogravimetric analysis

The amount of organic Sacrificial Passivation layer on the Ag and Cu particles (M%) and its decomposition temperature (T_d) were measured via Thermogravimetric analysis (TGA) in the Laboratory for Solid State Chemistry and Catalysis, at Empa Dübendorf at Netzsch DSC 404 Pegasus. The TGA is a thermal analysis method that records the mass changes of the sample. It allows identifying of physical and chemical properties of materials measured across range of temperatures or time (at constant heating rate, or constant mass loss, respectively). It is commonly used to gather information on properties like second-order phase transitions or decomposition [21]. For the purpose of the current evaluation, the amount of organic cap was defined as the total mass loss experienced by each sample when heated through 600 °C. The decomposition temperature was defined as the point of most rapid mass loss; represented as minima in the dM%/dT curve (Fig. 5.3). For this measurement the powders were weighted, placed in the alumina crucible on top of a thermocouple resting on a balance and heated at 20 °C/ min under He to 900 °C, as sample mass loss was monitored.
5.4. Differential Scanning Calorimetry

Sacrifically passivated powders of Cu or Ag were mixed in relevant composition with fine Sn powders and pressed. The powder mix compacts were prepared for evaluation by Differential Scanning Calorimetry (DSC) and tested at the Laboratory for Solid State Chemistry and Catalysis, at Empa Dübendorf at Netzsch DSC 404 Pegasus. The method records the heat flux proportional to the specific heat capacity in and out of the sample as compared to a reference material. The system is sealed into a chamber heated with a constant heating rate [22].

The passivated sets were prepared with the synthesized capped Ag and Cu particles and the non-passivated set with micron sized particles (Alfa Aesar). The binary powder mixtures were made by dry milling the Ag or Cu particles in air with Sn powder (Alfa Aesar) in a ratio of Ag-27 wt% Sn and Cu-60 wt% Sn, respectively. This composition was chosen to correspond with the Ag-Sn ε-phase (Ag₃Sn) and Cu-Sn η-phase (Cu₆Sn₅). The powder mixtures were pressed into particle compacts under 2 GPa and approximately 10 mg of each placed directly within the DSC. The DSC temperature profile consisted of two identical, consecutive scans characterized by heating and cooling rates of 20 °C/min and a maximum temperature of 300 °C. The set of DSC scans for the baseline particle com-
Impact is presented in Fig. 5.4. The Scan 1 was used to analyse how much Sn melted, Scan 2 shows the amount of re-melted Sn.

![DSC Scan Example](image)

**Fig. 5.4 – Example of quantification of the extent of the solid-state and liquid phase reaction (Sn melting endotherm) by consecutive Differential Scanning Calorimetry measurements.**

The endothermic peak is consistent with the melting of Sn at 232 °C. This set of scans is representative of all those obtained, where the Sn melting endotherm is prominent during the first scan and barely detectable when the sample is brought through the melting point of Sn during the second DSC scan.

### 5.5. Rutherford Backscattering Spectrometry

The composition of the multi-layered samples was determined by Rutherford Backscattering Spectroscopy (RBS). It is a non-destructive method allowing for the determination of the composition of a near surface layer of solid materials. The analysed sample is bombarded with ions at energy in the MeV-range (typically 0.5–4 MeV). The backscattered energy is measured with a solid state detector. The depth profiling of individual elements is provided by the energy loss of the ions in the material. The accessible depth for profiling is a couple of mm with a depth resolution of the order of 10 nm at the sample surface with 1% accuracy. The energy of an elastically backscattered particle depends on the mass of the target atom and on the depth at which the scattering took place [23][24][25][26][28]. These measurements were made using a 2 MeV and 5 MeV, perpen-
dicular to the sample He ion beam from the accelerator at the Laboratory for Ion Beam Physics, in the Physics Department, ETH Zürich. The energy distribution and yield of backscattered ions was recorded. The data obtained were compared with the simulated model using custom software package RUMP® and SIMNRA®. The simulated model is divided into several layers with variable concentration of involved elements. Combined optimization of the mass and depth resolution shows that a $^{4}$He beam with approx. 2 MeV backscattered under an angle close to 180° is usually most suitable [24]. The example of interpretation of the spectra is given in Fig. 5.5.

![Fig. 5.5 – Example of the interpretation of the depth scale data obtained and modelled by the RBS spectra.](image)

5.6. Auger Electron Spectroscopy

The Auger Electron Spectroscopy (AES) was used to support the composition analysis of nano-multilayers in as-deposited state. The method is an analytical technique using primary electron beam to probe solid surface. As a result of Auger processes, secondary electrons are emitted and their kinetic energy determined. The Auger electrons can only escape from the very first few monolayers (5-15 Å) what makes AES a very surface-sensitive technique [25][27]. The AES depth profile was performed on a Perkin-Elmer PHI 4300 SAM system operating with electron beam conditions of 5 kV and 35 nA beam current and using a CMA analyser. The depth profile calibration was done on SiO$_2$, and the sputter
parameters for the ion gun were: 2 kV ion beam, 4 nA ion current and sputter rate 0.635 nm per cycle.

5.7. Microscopic Investigation

Microscopic investigations were performed at:

- High Resolution Scanning Electron Microscopy in SE and BSE modes, equipped with EDS used for point analysis and mappings
  
  Hitachi 3500, FEI Nova NanoSEM 230, FEI ESEM XL30

- Transmission Electron Microscopy, with STEM, EDX mappings, bright field, dark field and diffraction mode
  
  JEOL 2200FS TEM/STEM, Philips CM30 TEM

- Atomic Force Microscopy for topographic information, in tapping mode
  
  Environment NanoScope AFM

Diversity of the samples required diverse techniques to be used:

- SEM cross-sections – conventional metallographic preparations with grinding on silicon carbide abrasive papers to a final grit of 2500 with water as a lubricant, followed up by polishing with a diamond paste (6 µm, 3 µm and 1 µm) on a woven polishing cloth with alcohol base lubricant and final polishing with 0.1 µm alumina suspension; no etching was applied.

- TEM cross-sections – lamellas made by Focused Ion Beam milling (Ga or He) or classical tripod method of mechanical polishing of a wedge shaped sample with a consequent Ar ion milling (Fishione Ion Mill), placed upon Au or Ni grid.

- Powder observations – for SEM and TEM, the powders were dried and spread across the Au or Ni grid with a membrane.
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Part 3 – Results and Discussion

The following Part 3 consists of the description, analysis and discussion of the results obtained for the control of the mass transport occurring between Cu-Sn and its application for rapid formation of interconnects. The chapters presented in this part respond to the major questions posted for the current study and contribute to the understanding and overcoming the restrictions of Cu-Sn system to enable rapid formation of interconnects. The chapters summarise the results and the discussions thereof in respect to: evaluation of Transient Liquid Bonding conditions in Cu-Sn system and characterisation of heating rate effect on the bonding behaviour (Chapter 6), development of a temporary diffusion barrier mechanisms and the characterisation of the liquid-solid interactions in such passivized systems (Chapter 7) and description of solid-state reactions and thermal redistribution of phases in nano-multilayer methodology (Chapter 8).

Chapter 6. Heating rate as an inhibitor of solid-state interdiffusion during joining of Cu and Sn

This chapter describes an assessment of the conditions of isothermal solidification (Transient Liquid Phase bonding) required to form metallurgical bond between Cu and Sn. The diffusion kinetics was assessed theoretically and the impact of heating rate condition on the solid interdiffusion is provided. The effect was evaluated experimentally and required infrastructure was designed.

6.1. Diffusion kinetics of Cu/Sn during isothermal solidification

The requirements given for the rapid formation of interconnect – low process temperature, short process duration or low cost materials provide a challenge for the scientific and engineering communities. The method described in the introductory Part 1, the Transient Liquid Phase (TLP) bonding with its isothermal solidification offers an answer upon these requests. The application of TLP bonding in Cu-Sn system requires basic consideration of processing temperature, interlayer thickness and time to completion. Additionally, heating rate was considered.

The processing temperature was defined by the upper limit for the industrial assembly. The resultant time to completion was the outcome of the relation of temperature and interlayer thickness based upon Second Fick’s Law (Eq. 6.1) [1].
Under assumption of pure liquid-solid interaction, the analysis of the reaction kinetics between Cu-Sn is given in the Fig. 6.1.

\[ t_c = \frac{(h^2)}{16K^2D_0}\exp\left(\frac{Q}{RT}\right) \]  

(Eq. 6.1)

where \( h \) – interlayer thickness; \( K \) – non-dimensional parameter depending on the solubility of Sn in Cu and the concentration of Sn in the interlayer; \( D_0 \) and \( Q \) – the interdiffusion constants for the Cu solid solution; \( R \) – gas constant; \( T \) – absolute temperature of process.

At single temperature, i.e. 270 °C the estimated time to completion of the interdiffusion of 10 µm thick interlayer is in the range of 300 h. The calculation also indicates that it is (theoretically) possible to form a TLP bond in the time frame of 120 s, when the interlayer thickness is kept up to 100 nm.

The literature indicates a potentially large impact of the heating rate on the TLP processing time [1]. Fig. 6.2 provides a theoretical interpretation of this effect derived from (Eq. 6.2). The data values used for the calculation were taken from the previous study [3][4]. The relation indicates that at the lowest temperature for any heating rate, the reaction between Cu and Sn requires the longest processing time for the bond formation.
where: $K$ - non-dimensional parameter that depends on the solubility of Sn in Cu and the concentration of Sn; $D_0$ and $Q$ - the interdiffusion constants; $R$ - gas constant; $T$ – absolute temperature of bonding; $T_r$ - heating rate, $k$ and $n$ are the constants.

\[ t_c = \frac{1}{D_0} \left( \frac{3k(\Delta T / T_r)^n}{8c_r K} \left( \frac{\rho_{Sn}}{\rho_r} \right) \right)^4 \exp \left( \frac{Q}{RT} \right) \]  
(Eq. 6.2)

However, at increased heating rates the process time needed for the bond formation is in the (industrially accepted) range of minutes, even for the lower temperatures. To this date, no experimental study has however evaluated such an effect. This thesis has approached the open points. The joining experiments were performed at high heating rates. The precisely controlled heating rates was achieved through design and manufacturing of the laboratory scale Rapid Thermal Annealing furnace.

6.2. Rapid Thermal Annealing Furnace – purpose and design

The Rapid Thermal Anneal (RTA) furnace was designed to provide for rapid, exact heating and cooling of small samples under an inert or forming gas environment. This device provides for thermal treatment and joining experiments. The distinct feature is its extremely high heating and cooling rates enabled by the use
of high intensity infrared lamps as the heat source. In regard to requirements, the suitable commercially available solution was not present. Therefore, for the purpose of the work, the Rapid Thermal Annealing (RTA) furnace was designed and custom assembled in-house as shown in Fig. 6.3.

The heating is achieved via two 1000 W infrared lamps, which are aimed at a SiC susceptor. This susceptor absorbs the electromagnetic radiation of the lamps converting it into heat, which in turns heats the sample placed upon it. Since all other materials within the furnace are transparent or reflecting to the lamps radiation, only the mass of the susceptor and sample are heated thereby providing extremely high heating rates.

The heating characteristic was verified with different proportional-integral-derivative controller setups and tested at set points from 50 to 400 °C and heating rates up to 350 °C/min. In Fig. 6.4 a precise characteristic of the heating and
cooling behaviour of the RTA furnace is given. Regardless of the set point, the heating rate follows precisely its’ designed characteristics.

![Fig. 6.4 – Heating characteristics of the RTA furnace for 20, 150 and 350 °C/min and set point varying from 120 to 250 °C.](image)

The detailed specification is given in the Appendix I.

6.3. Growth mechanism of intermetallic compounds in Cu-Sn during isothermal solidification at rapid heating conditions

The correlation between the process duration (time to completion) and the Sn thickness as well as the theoretical effect of the heating rate were discussed in the Section 6.1. The expected heating rate effect was therefore investigated on the standard joint geometry Cu/Sn/Cu with use of the Rapid Thermal Annealing Furnace according to the experimental design provided in Section 4.2.1 of in the Methodology. The results presented here are summarised in [15]. Allowing the same dwell time and set point, the heating rate effect on the Cu/Sn/Cu joint formation is clearly observed. The heating time for the 20 °C/min is 660 s (11 min), for the 350 °C/min – 38 s. The rapid heating prevents the initial solid-state reaction at the Cu/Sn interface and allows for the direct contact of solid Cu surface with liquid Sn and the subsequent rapid dissolution (heterogeneous solid-liquid
reaction) thereof. Similar interaction happens during wave soldering process when the circuits run through the liquid bath of Sn [16]. The cross-sections of the resulting microstructures for most extreme cases – at the heating rate for 20 and 350 °C/min, annealed at 250 °C 3 min, are compared in the following Fig. 6.5.

![Cross-sections of Cu/10 μm Sn/Cu TLP bonds produced at 250 °C during 3 min dwell at 20 and 350 °C/min heating rate, BSE, 15kV.](image)

Despite the same initial Sn thickness, dwell time and set point, the resulting microstructures for low and high heating rates differ. Both conditions lead to the expected formation of scallop like Cu₆Sn₅ and thin flat layer of Cu₃Sn, as well as voids at the initial interface position. The scallop morphology is driven by thermal grooving. For the low heating rates the growth of Cu₆Sn₅ scallops is smaller and significant amount of Sn is left in-between Cu surfaces. For the high heating rates, on the contrary, only small pockets of Sn are surrounded by Cu₆Sn₅ grains. Fig. 6.6 gives a comparison of the deep-etched samples showing the cavities after etched out Sn.

Interestingly, the behaviour is consistent with the theoretical expectation. The rapid heating rate allows for the initial interdiffusion interaction between solid Cu and already liquid Sn. Therefore, allowing high solubility and diffusion rates. The low heating rate however enables an IMC formation already during solid-solid interactions. Such formed layer hinders the mass transport over the inter-
face and slows down dissolution of Cu in liquid Sn once the melting point is reached.

Fig. 6.6 – Comparison of microstructures of Cu/Sn/Cu TLP joint produced at 250 °C during 3 dwell at 20 and 350 °C/min heating rate, BSE 15kV, deep etched.

Fig. 6.7 and Fig. 6.8 give an overview of the microstructure evolution during different stages of dwell time (30 s, 3 min and 10 min) at 250 °C at 20 and 350 °C/min heating rate. For the low heating rate of 20 °C/min initial nucleation of Cu₆Sn₅ at the Cu/Sn interface is observed and the planar layer growth is seen. With progressing dwell time, the Cu₆Sn₅ growths in scallop form, and the Cu₃Sn continuous layer is seen at the Cu/Cu₆Sn₅ interface. For the high heating rate of 350 °C/min the Cu₆Sn₅ is seen at the initial Cu/Sn interface but also in the Sn volume. With the annealing time, the Cu₆Sn₅ proceeds to growth consuming Sn, and Cu₃Sn appears at the Cu/Cu₆Sn₅ interface. The samples observed after 30 s annealing showing the IMC nucleation away from the Cu/Sn interface were deep etch to remove not consumed Sn and investigate if the three-dimensional structure of the IMC grains.
Fig. 6.7 – Overview of microstructure evolution for Cu/Sn/Cu TLP joint produced at 250 °C during 0.5, 3 and 10 min dwell at 20 °C/min heating rate, BSE 15kV.
Fig. 6.8 – Overview of microstructure evolution for Cu/Sn/Cu TLP joint produced at 250 °C during 0.5, 3 and 10 min dwell at 350 °C/min heating rate, BSE 15kV.
Based on the metallurgical evaluation the behavioural regimes in the bond formation mechanism can be observed. These mechanisms were evaluated and described for different heating rates. The joint formation at the low heating rates is consistent with the literature data [5-9]. The conventional IMC growth during the TLP process occurs through the initial nucleation and later growth of Cu₆Sn₅ phase at the Cu/Sn interface. The TLP at low heating rates follows this path (Fig. 6.9 (a)). The interfacial growth of the IMC leads to the complete consumption of Sn into IMC, if the time to completion is long enough. A different path is however seen for the Cu-Sn bonding at the rapid heating rates.

![Diagram](image1)

Fig. 6.9 – Illustration of the TLP mechanism at (a) low heating rate – at 20 °C/min the interfacial growth of the IMC leads to the bond formation, (b) high heating rate – at 350 °C/min the interfacial growth is complimented by precipitation growth from the bulk of the liquid Sn pool.

At the heating rates of 350 °C/min, the interfacial IMC growth of Cu₆Sn₅ occurs parallel to the homogenous nucleation away from the interface. It is most likely caused by increased dissolution and saturation of the Cu in liquid Sn (caused by the interfacial consumption of Sn and the liquid Sn is supersaturated by Cu). The mechanism is presented in (Fig. 6.9 (b)). It starts by dissolution and saturation of the Cu in liquid Sn, parallel with intermetallic precipitations/nucleation in liquid Sn (Fig. 6.9 (b1)). It is followed by the initial interfacial IMC formation (Fig. 6.9 (b2)) that continues its growth from the internal (precipitations) as well as interfacial IMCs (Fig. 6.9 (b3)), to be completed when Sn is entirely consumed (Fig. 6.9 (b4)).
The preferential dissolution at the grain surface that is in contact with liquid Sn is limited and the grooving is not promoted to form typical scallop-like structure [14]. The joint formation is, by definition, a non-equilibrium process. The system is strongly shifted from its equilibrium state through heating, dwelling and cooling stages. Heating rate affects not only the solid-state interaction but also the melting behaviour of the material. The rapid heating realised by pulsed laser beam has been proven to affect the melting temperatures and in particular enthalpy of melting for semiconductor materials [2][13]. The rate, with which the interfacial reaction in Cu/Sn system reaches the equilibrium, depends on the diffusion path. The diffusion of the Cu in Sn is 5 to 6 order of magnitude higher [3]. The kinetic should not create limitations for the process form structural point of view. However, the coalescence can be limited by the driving forces in the diffusion zone. In the conventional interfacial TLP mechanism [5][6][7], the IMC forms at the Cu/Sn interface and the slow transport of Cu and/or Sn through the IMC layer allows its further growth and the dissolution occurs at GB [14]. This determines the process with the diffusion rate in the IMC that is slowed down since the diffusion of mobile species in the solid increases with time.

In the timeframe, between the initial contact and the interfacial IMC formation, the dissolution of the Cu in liquid Sn is present, what is commonly neglected in the literature. Activating surface Cu (or overheating) of the Cu/Sn interface can shift focus of process determination on the Cu dissolution stage [10][16]. Fig. 12 shows the theoretical heat flow diagrams based on the metal conduction properties for different dwell times. It indicates the strongest overheating at the interface from the heat source. The crucial point in this mechanism is the local supersaturation of the Cu in liquid Sn, later formation and increase growth of the nucleated IMC within Sn phase. According to the phase diagram saturation limit of solid state dissolution of the Cu in Sn is around 5 at.% at 250 °C.
Fig. 6.10 – Heat flow diagrams in the samples from the direct heat source (through metal conduction).

The much thinner interfacial IMC is formed and occurrence of the voids on the border of the interfacial and ripened precipitate IMC is observed experimentally. It is indicated that the precipitates growth does not exclude formation of interfacial IMC, however the thickness of the interfacial IMC is affected by competitive nucleation and growth of the precipitating IMCs. The thin interfacial IMC promotes quicker dissolution of Cu, which is known to diffuse quickly through Sn via interstitial mechanism. This is promoted by the large overheating caused through rapid heating and shortens the time to completion during the TLP. There are potentially few reasons of the superdissolution/supersaturation of Cu in liquid Sn. It could be caused by the interface overheating due to the differences in thermal conductive coefficient or different diffusion mechanism in the dynamic interface between the Cu lattice and molten solution. An additional aspect is the surface preparation before bonding. However, the observed behaviour of the bond formation is directly linked to the heating rate applied.
6.4. Rapid interconnect formation using heating rate approach in wafer-level-bonding configuration

The successful control mechanism of the solid state interaction within a joining scheme was given with the setup of rapid heating rates during bonding of Cu-Sn in sandwich geometry in Rapid Thermal Annealing furnace. The rapid heating during Transient Liquid Phase (TLP) bonding as also validated with wafer-level-packaging approach. The Si chips with Sn bumps and Cu metallization were obtained from IMEC, Belgium in the frame of EU Project Fab2Asm [11]. Based on the geometry of the microelectronic chips a simplified set of 2.5 μm Cu and 850 nm Sn on 5 nm Cu (for adhesion) films were deposited on separate Si/SiOx/SiNx/TaN wafer to simulate chip bonding on a larger area (Fig. 6.11).

![Fig. 6.11 – Schematic of (a) chip geometry, (b) simplified test sample.](image)

Fig. 6.11 presents a reference micro bump after 2 min at 300 °C after 350 °C/min heating rate. An EDX mapping presents the composition of the bump of Sn (blue), Cu (red) and Si (green), the overlap between the Sn and Cu is an IMC phase of the composition close to Cu₆Sn₅, more Sn and Cu rich regions are seen at each of the Si wafer.

![Fig. 6.12 – SEM image and EDX mapping of the bonded IMEC chip, at 2 min at 300 °C after 350 °C/min heating rate, 15 kV.](image)
Fig. 6.13 shows similar treated model sample. The two parts were clamped together with a holder and heated at 300 °C during 2 min with 350 °C/min in the RTA oven. The cross-section seen (Fig. 6.13) was achieved upon cleavage of Si chips after joining; therefore quantitative chemical analysis could not be performed. Nonetheless, there is a clearly seen region of well-formed grains of Cu-Sn mixture, most likely IMC phase. The initial Sn/Cu interface is not recognizable.

![SEM image of the cleaved Si/2.5 μmCu/0.85 μm Sn/5nm Cu/Si sample, at 2 min at 300 °C after 350 °C/min heating rate; 15 kV.](image)

Fig. 6.13 – SEM image of the cleaved Si/2.5 μmCu/0.85 μm Sn/5nm Cu/Si sample, at 2 min at 300 °C after 350 °C/min heating rate; 15 kV.

**Conclusion**

In order to be practical for microelectronic assembly the TLP bonding should be ideally implemented in a short time at relatively low temperatures.

Through the course of this research it has been shown that the time required to formulate a TLP connection between Cu and Sn strongly depends not only on the initial Sn thickness and the time required for the consumption of intermediate phases (that scales with the initial Sn thickness), but it can also be influenced by the process conditions other than the set point.

Moreover, this work for the first time gives the experimental evidence of the effect of the heating rate onto the bond formation mechanism in the Cu-Sn system. The observed critical heating rate was at 350 °C/min. Furthermore, with this analysis, the process window needed for rapid formation of interconnects within
the TLP scheme has been significantly enlarged. The joint of 0.85 μm Sn were successfully obtained in industrial conditions at 2 min at 300 °C, with 350 °C/min.

Current work has also demonstrated that the heating rate affects the IMC growth mechanisms, what could potentially eliminate the mechanical integrity issues of Cu-Sn bonds due to accumulation of voids at the centre line of the joint. Therefore, upon the theoretical assessment of the diffusion kinetics in the Cu-Sn isothermal solidification, the effect of the heating rate on the bond formation in bulk Cu-Sn system was confirmed experimentally through the design, setup and application of Rapid Thermal Annealing Furnace.
Bibliography


[3]. M. Pawelkiewicz, J. Janczak-Rusch, M. Danielewski, “Kinetic growth behaviour of compound layers in the Sn-Ag-Cu system using the diffusion multiple technique”, in submission


Chapter 7. Inhibition of solid-state interdiffusion with an application of temporary diffusion barrier coating

The overall objective of this work is to address the diffusion control between Cu and Sn and to formulate a methodology for rapid formation of interconnects. The specific results discussed through this chapter concern the effect of hindering the solid-state interaction through an application of Sacrificial Passivation. The term Sacrificial Passivation describes an organic coating that hinders interaction between the metallic components for a certain time and/or up to a certain temperature, upon which its behaviour is “deactivated” to allow the reaction to proceed [1]. Sacrificial Passivation was incorporated as a kinetic barrier between Cu and Sn and between Ag and Sn as a control. The passivation study was performed to characterise the reaction kinetics of the passivated system.

7.1 Formulation of Sacrificial Passivation for the bulk behaviour characteristics

Sacrificial Passivation in form of organic thin film was poised to hinder the solid-state interaction between joined interfaces. A characterisation of the coatings in terms of their application was performed. A coatability study was used to assess the thickness and uniformity of the films. The study was focused on poly vinyl alcohol (PVA), a water soluble polymer. The polymeric layers were spin coated over a piece of Si wafer with a resulting thickness as a function of the concentration of the polymer solution and the rotation speed. The PVA samples yielded homogeneous and transparent coatings. The calculated standard deviation indicated the uniformity of the coated layer. The colouring varied with thickness from clear transparent to bluish. The ellipsometry measurements confirmed that the thickness of the layer depends on the concentration of the polymer in the solution and on the spin rate. Since there was no measurable difference in thickness between depositions at 30 s or 60 s, the results for 60 s spin time are reported. The thickness of the PVA films was between 48 nm for 3% PVA/H₂O solution at 5000 rpm, and 11 nm for a 1% PVA/H₂O solution at 5000 rpm, and below 5 nm for a 0.5% PVA/H₂O solution at the same rpm. The highest thickness of 80 nm was measured for coating obtained from 3% PVA/H₂O solution at 2000 rpm.
The effect on the thickness correlated with higher solution concentrations and with spin rate.

7.2 Characterization of reaction kinetics in sacrificially passivated Cu-Sn and Ag-Sn diffusion couples

The passivation study of the barrier behaviour of Sacrificial Passivation was performed in the diffusion couple geometry. The study was conducted for the Ag-Sn and the Cu-Sn systems, with the PVA chosen for Sacrificial Passivation based on the formulation study performed for the uniform and reproducible coatability. The PVA passivation film of 80 nm was applied on the polished Ag and Cu surfaces and pressed against polished Sn coupon forming a diffusion couple (Fig. 7.2).

The passivated Ag/Sn and Cu/Sn sandwiches were heated according to a previously established thermal profile and kept for 30 h at 200 °C under vacuum. The annealing at 0.95 Tₘ(Sn) was setup to allow for slow degradation of Sacrificial Passivation and enable a direct contact between the passivated surfaces. The observation of the interface evolution was compared to non-passivated samples. A
very limited IMC formation at the position of the initial interface was observed for the passivated diffusion couples between Ag/Sn and Cu/Sn after 30 h of annealing at 200 °C. In both cases, the interface was porous at the initial interfacial location, most likely due to the residues of the passivation. Fig. 7.3 (a) represents the passivated interface of Ag/Sn couple. From the observation, the intermetallic compound at the interface is fragmented and very limited, when compared to the non-passivated sample. Fig. 7.4 depicts passivated interface of Cu/Sn couple, revealing two intermetallic compounds formed. The intermetallic phases formed were confirmed with qualitative EDX measurements as: Ag₃Sn for the Ag/Sn interface and Cu₃Sn, Cu₆Sn₅ for the Cu/Sn interface, which is consistent with the state of the art information [11][13].

The intended effect of the Sacrificial Passivation as a kinetic barrier was observed for Ag-Sn system. The calculated growth rate for non-passivated and passivated couple were: 1.1x10⁻⁴ µm/s and 9.25x10⁻⁶ µm/s, respectively. The average IMC layer thickness is derived from the ratio of the IMC area divided by the interface length. The growth rates indicate that the reaction between Ag and Sn was successfully hindered.

![Fig. 7.3 – SEM image (SE) of the non-passivated and passivated Ag/Sn interface in the diffusion couple configuration, after 30 h at 200 °C.](image)

The Cu-Sn interfacial reaction was not affected by the presence of the kinetic barrier layer. In fact, the growth rates (for IMC layer consisting of Cu₃Sn and Cu₆Sn₅) are comparable for both passivated and non-passivated samples with 4.61x10⁻⁵ µm/s and 5.09x10⁻⁵ µm/s respectively. The growth rates of the specific intermetallic compounds were not compared. The differences in appearance of
Cu$_3$Sn layer between non-passivated and passivated sample (Fig. 7.4) may arise from reaching the equilibrium earlier, when the passivation layer is not present. The passivation affects also the internal porosity at the location of initial interface. The growth rate of the single binary phase is determined by the mobility of atoms and the Gibbs energy of the phase formation (chemical reaction). The interface kinetics is described by the linear-parabolic growth for the single phase growth. When the initial phase in thin, the growth rate depends purely on interface transport [2]. When the thickness of the growing phase rises (parabolic reaction period) the process is controlled by bulk diffusion. There is an intermediate reaction period, where a transition from an interface-controlled process to a diffusion-controlled (from linear to parabolic rate law) occurs.

Typically, the growth rate of the Cu/Sn and Ag/Sn IMCs follows a parabolic kinetics [3][4][5]. The PVA kinetic barrier of Sacrificial Passivation is effective for the Ag/Sn couple and successfully limits and inhibits the rate of the interfacial reaction. In contrast, the reaction rates of the Cu/Su couple were not affected. The bulk passivation study confirmed that Sacrificial Passivation in form of PVA is successful for the Ag/Sn couple, but not for the Cu/Sn.

7.3 Control of solid-state diffusion as the method to reduce the relevant diffusion distance

For joining schemes, the literature offers shortening of diffusion distance with extending surface of the contact area between the components, through use of pow-
der [8][9]. Reducing the relevant diffusion by the infiltration of base metal powder compacts with liquid filler in an attempt to accelerate joining kinetics was implemented for Ni-based superalloys [6] and Ti-alloys [7]. This technique, however, was not applicable to material systems, where fast kinetics of the interfacial reaction occurs. The consequence of such an approach for powder mix of low melting point metals, like Sn and high diffusivity metals like Cu (or Ag) is the solid-state consumption of the Sn prior melting. The reduction of diffusion distances with the incorporation of this temporary kinetic barrier is only practical for sintered powder mix. Therefore, the approach was focused around the ability to synthesize organically capped nano-scale metal particles as the base material. The organic cap was successfully anticipated to inhibit the solid-state reaction between adjacent particles and, if appropriately matched, its timely decomposition allows the subsequent liquid phase reaction to proceed uninhibited. The following sections describe the subsequent results. The approach allowed stabilisation of fine powders (100-300 nm particles), but required the formulation and understanding of the synthesis procedures and the products thereof.

### 7.3.1. Investigation of thermal stabilisation of Sacrificial Passivation over synthesised metallic particles

The motivation to minimise diffusion distance while preventing the interfacial reaction between the components, formulated the approach to use passivated powder mix compacts. To hinder undesired solid-state interaction between the particles, in-situ encapsulation was incorporated. The thermal responses of the system were therefore studied.

#### Synthesis of passivated Ag particles

The chemical synthesis was used to encapsulate Cu and Ag particles with Sacrificial Passivation [10]. The details of the approach are described in Chapter 4.2.2. Despite the variance in appearance, XRD results in as-synthesised state confirm that all samples yielded Ag particles. The lattice constant calculated for this set of planes is 4.08 Å, a value in agreement with Ag. Pressed samples were heated with 20 °C/min up to 300 °C and cooled. The XRD analysis of these samples showed counts distribution for diffraction peaks in agreement with expected Ag powder diffraction. The images in Fig. 7.5 (a) show the non-dispersed Ag/PVP particles in porous clusters. Fig. 7.5 (c) describes dispersed, round particles with
diameter in 100-300 nm range. The TEM images also illustrate that the particles are successfully encapsulated with a 10-20 nm thick organic layer.

![Image](a)

![Image](b)

![Image](c)

Fig. 7.5 – (a) SEM image of non-dispersed Ag/PVP particles, (b) XRD pattern and (c) TEM images of dispersed Ag/PVP particles (sample type 7).

TGA experiments provided the decomposition temperature $T_d$ of the organic cap (as exemplary charts in Fig. 7.6 for Ag/PVP sample). For the purpose of the current evaluation, the decomposition temperature, the point of most rapid mass loss is represented as minima in the $\mathrm{dM}/\mathrm{dT}$ curve.

When comparing the results to the similarly measured $T_d$ for each of the organic molecules themselves – 485, 295 and 240 °C (PVP, PVA and SDS respectively), it has been observed that the $T_d$ of the organic cap on the particle can be influenced by the procedural factors and can be steered according to the requirements.
Fig. 7.6 – TGA graph showing decomposition temperature and mass loss of Ag/PVP particles (sample type 7) over the heating rate at 20 °C/min up to 900 °C. While most of the measured decomposition temperatures for the organics on the particles fall in this regime, quite different behaviour from the molecules themselves was observed. For instance, the sample capped with PVA showed the lowest decomposition temperature of 252 °C, lower than the decomposition temperature measured for the polymer (T_d PVA was measured 295 °C). The SDS capped particles exhibited the widest range of decomposition temperatures from 265 to 507 °C (whereas the T_d SDS was measured at 240 °C).

Tab. 7.1. – TGA data on decomposition temperature and mass loss of in-situ encapsulated Ag particles according to DOE

<table>
<thead>
<tr>
<th>sample</th>
<th>factor</th>
<th>decomposition temperature Td (°C)</th>
<th>rate (ml/min)</th>
<th>mass loss (M%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a PVP</td>
<td>493</td>
<td>50</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td>a PVA</td>
<td>504</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>a SDS</td>
<td>507</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>b PVP</td>
<td>506</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>b PVA</td>
<td>274</td>
<td>50</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>b SDS</td>
<td>336</td>
<td>5</td>
<td>0.8</td>
</tr>
<tr>
<td>7</td>
<td>c PVP</td>
<td>443</td>
<td>5</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>c PVA</td>
<td>252</td>
<td>0.5</td>
<td>2.42</td>
</tr>
<tr>
<td>9</td>
<td>c SDS</td>
<td>265</td>
<td>50</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The results are summarised in the Tab. 7.1. The trends of T_d with both ratio and rate appear to reach an optimally high value with their middle level indicating
the interaction between those parameters. Fig. 7.7 shows the values of $T_d$ and mass loss $M\%$ for chosen synthesis scenarios.

![Graphs showing decomposition temperature and organic mass loss](image)

Fig. 7.7 – Response plots for (a) decomposition temperature and (b) organic mass loss of the Sacrificial Passivation on Ag particles in regards to different procedural factors of the synthesis used – synthesis type, organic molecule, molar ratio and addition rate.

The linear graphs were introduced to facilitate the assignment of the experimental results. Two response plots were generated that illustrate the influence of the procedural factors and their levels onto the amount of organics and the decomposition temperatures (Fig. 7.7). The responses plotted for each factor and level represent the average value yielded for samples with that common factor and level. For instance, the $T_d$ response for the factor of addition rate at level 5 ml/min is calculated by averaging the decomposition temperatures for trials with this specific addition rate level (trail 2, 6 and 7 as given in Tab. 7.1). The responses of synthesis and organic used are connected by dashed lines to signify that the apparent numerical trend does not exist within these factors. The $T_d$ of the organic cap is heavily influenced by the variation of procedural factors and levels. The synthesis route influences $T_d$ most significantly with Route a (EG) providing for the highest response and Route c (Glucose) for the lowest. The next most influential factor is the organic molecule. While the highest response is achieved with PVP as the capping agent, the lowest is achieved with PVA even though its native $T_d$ of 295 °C is 55 °C higher than that of SDS. The trends of $T_d$ with both ratio and rate appear to reach an optimal high value with their middle level. For molar ratio, the strongest influence is with the lower levels and the trend is for higher $T_d$ with an increasing ratio. For the addition rate, the influ-
ence is strongest with its higher levels, indicating the lower $T_d$ with higher rates. An additional explanation for the apparent high optimum of ratio and rate at their midlevel is the presence of the interaction between both ratio and rate. The evidence of this interaction is present for the sample synthesised with PVA in Glucose environment, at low ratio at low additional rate (trial 8). For this trial all the factorial levels where at their optimum value for a low thermal response ($T_d = 252 \, ^\circ C$) but the addition rate. When an interaction is present, the levels of the interacting factors do not follow the DOE prediction.

Varying the parameters of the synthesis between (i) – synthesis route (ethylene glycol (EG), ascorbic acid or glucose based); (ii) – organic molecule (Polyvinylpyrrolidone (PVP), Poly(vinyl alcohol) (PVA) and Sodium dodecyl sulphate (SDS)); (iii) – molar ratio of the precursor metal salt to organic molecule and (iv) – addition rate of the metal salt to the reaction mixture, tuned the thermal response of the passivation layer. The $T_d$ of the organic cap was strongly influenced by the variation of procedural factors and levels. As described for the ratio and rate the middle values yield highest effect onto $T_d$. However, they did not yield with the highest $T_d$ response, when they were used in combination. An explanation for the apparent optimum of ratio and rate at their midlevel is the presence of an interaction between those two factors. This issue was investigated further to establish steering parameters for obtaining the exactly tailored thermal behaviour of the passivation. The additional set of experimental trials characterizing the interaction varied only in the molar ratio = 0.5 and 5, and addition rate = 0.5 and 50. Since the approach of the whole study was to control the interaction in the solid state, the opportunity to in-situ tailoring of desired properties according to the requirements was further pursued. The levels of synthesis and organic were chosen as to minimize the $T_d$ response. The synthesis route was glucose based, and the organic molecule investigated as the capping agent was PVA, since it has been shown suitable for Ag/Sn passivation.

The obtained particles showed an encapsulation $T_d$ in the range of 191 °C and 375 °C, where the value for the PVA molecule itself is 295 °C. The interaction between the factors of ratio and rate was herewith confirmed. The lowest decomposition temperature of the investigations ($T_d = 190^\circ C$) was obtained for ratio 5, rate 50. Fig. 7.8 shows the plots of rate response at different molar ratio.
The decomposition mass is mostly influenced by the chosen synthesis route. The routes a (EG) and b (ascorbic acid) provided similar responses of 0.7 M% and 0.9 M% respectively, while Route c (Glucose) yielded 2.8 M%. The type of organic shows less of an impact and was calculated for PVP at 1.6 M% and for PVA and SDS at 1.4 M%. The decomposition mass increased with both increasing ratio and addition rate. The maximum value was reached in the combinatory trial (Fig. 7.8). This confirms that M% is not affected by the interaction between the procedural factors. With this result, the M% can be easily tailored upon demand. With the Taguchi based DOE, the thermal behaviour of Sacrificial Passivation for Ag powders is therefore proven tuneable by the selection of the synthesis conditions.

Synthesis of passivated Cu particles

A similar approach was chosen for encapsulating Cu particles. The effect of kinetic barrier on the thermal stability was studied by synthesising Cu particles encapsulated in different organics. The synthesis of Cu was confirmed with XRD.
The TEM shot of dispersed Cu/PVP particles is given in Fig. 7.9. For each synthesis, the particles have a diameter between 150-400 nm, are discrete and roundish in shape. The TGA experiments provided the decomposition temperature $T_d$ of the organic cap (as Fig. 7.10).

The $T_d$ of the organic cap is strongly influenced by the variation of procedural factors and levels. The trends of $T_d$ with both ratio and rate appear to decrease. The addition rate shows a stronger impact on the $T_d$ response. Tab. 7.2 summarises the values of $T_d$ for investigated scenarios. The response plots are given in Fig. 7.11. The particles encapsulated with PVP show higher $T_d$ responses than the ones with SDS. However, the trials yielded particles with the encapsulation $T_d$ in
the range of 485 °C. However for the SDS, the range of \( T_d \) is between 300 and 480 °C, whereas the SDS molecule itself decomposes at 240 °C. Interestingly, the \( T_d \) rises with molar ratio for the addition rate of 5 ml/min, and decreases with molar ratio for the addition rate of 50 ml/min. This illustrates the specific interaction between the procedural factors (Fig. 7.12). According to the response plot, the factors chosen for the test sample synthesised with PVP, low ratio and low addition rate should yield the highest \( T_d \) response, which has been confirmed with TGA at 487 °C. Similarly, the condition for the test sample synthesised with SDS, high ratio and high addition rate should and do yield the lowest \( T_d \) response (300 °C).

Tab. 7.2. – TGA data on decomposition temperature and mass loss of in-situ encapsulated particles according to DOE

<table>
<thead>
<tr>
<th>sample</th>
<th>organic</th>
<th>factor ratio</th>
<th>rate (ml/min)</th>
<th>decomposition temperature ( T_d ) (°C)</th>
<th>mass loss (M%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 PVP</td>
<td>0.5</td>
<td>5</td>
<td>487</td>
<td>93.12</td>
<td></td>
</tr>
<tr>
<td>2 SDS</td>
<td>0.5</td>
<td>5</td>
<td>302</td>
<td>94.40</td>
<td></td>
</tr>
<tr>
<td>3 PVP</td>
<td>0.5</td>
<td>50</td>
<td>482</td>
<td>95.68</td>
<td></td>
</tr>
<tr>
<td>4 SDS</td>
<td>0.5</td>
<td>50</td>
<td>485</td>
<td>92.37</td>
<td></td>
</tr>
<tr>
<td>5 PVP</td>
<td>5</td>
<td>5</td>
<td>480</td>
<td>92.70</td>
<td></td>
</tr>
<tr>
<td>6 SDS</td>
<td>5</td>
<td>5</td>
<td>438</td>
<td>88.00</td>
<td></td>
</tr>
<tr>
<td>7 PVP</td>
<td>5</td>
<td>50</td>
<td>485</td>
<td>94.16</td>
<td></td>
</tr>
<tr>
<td>8 SDS</td>
<td>5</td>
<td>50</td>
<td>300</td>
<td>99.42</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7.11 – Response plots for (a) decomposition temperature and (b) organic mass loss of the Sacrificial Passivation on Cu particles in regards to different procedural factors of the synthesis used – organic molecule, molar ratio and addition rate.
The second highest $T_d$ response (485 °C) was observed for SDS encapsulation with the combination of low molar ratio and high addition rate. This is confirmed by the highest interaction response evaluated. Furthermore, using SDS as a cap, which has a low Td, enhances the interaction effect generated by the other factors.

Fig. 7.12 – Response plots for decomposition temperature of the SDS Sacrificial Passivation on Cu particles in regards to different levels procedural factors – addition rate and molar ratio interaction.

The thermal behaviour of Sacrificial Passivation for Cu powders is therefore proven tuneable with the synthesis conditions.

The synthesis procedures set for Ag and Cu particles synthesis were established and characterized. The reduction synthesis methodology is simple, yet successful when enhanced with Taguchi Experimental Design. The DOE via Taguchi allows fewer experiments for Ag and provided useful result analysis tool for both Ag and Cu. Using Cu particles, the interaction between molar ratio and addition rates was characterized as heavily influencing $T_d$ and M%. Moreover, the use of the Cu interaction has led to predictions in the optimization and minimization of $T_d$ and M% in Ag.
7.4 Quantification of solid-state reaction in sintered Cu-Sn and Ag-Sn powder mix compact

Even though the main emphasis of this work is on Cu-Sn, the Ag-Sn provides the reference information on the reactive diffusion and hindering solid-state interaction. The in-situ encapsulation method of metallic particles with Sacrificial Passivation was chosen as a route to preclude solid-state interdiffusion, yet to allow the subsequent liquid phase reaction to proceed uninhibited. The assembly of the alloy constituents with encapsulated fine metal particles was performed (Fig. 7.13). To understand the passivation ability of the organic capped systems Cu-Sn and Ag-Sn, the study using DSC as a measurement technique was performed1.

![Fig. 7.13](image)

**Fig. 7.13** · Illustration of (a) encapsulation of metallic particles with Sacrificial Passivation; (b) constructed compact of powder mix.

The amount of liquid phase formed in the particle compacts during DSC scans was quantified by calculating the area under the corresponding endothermic peak – $\Delta H_{\text{actual}}$. This value was compared to the theoretical value for Sn – $\Delta H_{\text{Sn}}$. The two sequential DSC scans provided the wt.% of Sn initially available to form a liquid phase in the particle compact – $X_{\text{Sn}}$(scan nr 1) and fraction of the unreacted Sn (scan nr 2):

1 The results of this study for Ag-Sn system was published in parallel to the current work [1]. The results presented in this thesis are reproduced samples based on that study.
This expression used for the first DSC scan quantifies the amount of Sn consumed by solid-state reaction prior to reaching its melting point – formation of intermetallic compound, as defined by the baseline scan for the compact without passivation. The same expression used for the second DSC scan indicated the subsequent solid-liquid phase reaction [1].

The results of Sn melting for both systems are summarised in Fig. 7.14 (Ag-Sn) and Fig. 7.15 (Cu-Sn). For the Ag-Sn compact in the first DSC run, the baseline yielded 37 wt.% consumption of the initial Sn available. In contrast, for the PVP and PVA encapsulation the 34 wt.% and 35 wt.% were achieved. For the SDS capped particles, however, the theoretical value of the Sn melting endotherm was achieved suggesting the solid-state reaction did not occurred and therefore the successful passivation was achieved. For the second DSC run, for the baseline a very limited endothermic reaction is detected (< 5 %ΔH_{Sn}) for the baseline. Similar level was seen for PVA and SDS coated particles. This result indicated that nearly all of the Sn initially present was converted into a higher melting point phase over the course of the scan nr 2.

For the PVP encapsulated samples the level of over 20 % of the initial Sn present is un-reacted and therefore available to form a liquid phase.

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![Normalized heat of fusion of Sn based on DSC scans for chosen Ag-Sn.](image)

<table>
<thead>
<tr>
<th>sample</th>
<th>factor-route</th>
<th>organic</th>
<th>ratio</th>
<th>rate</th>
<th>%ΔH_{Sn} DSC run 1</th>
<th>%ΔH_{Sn} DSC run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>62.50</td>
<td>2.80</td>
</tr>
<tr>
<td>7</td>
<td>c</td>
<td>PVP</td>
<td>5</td>
<td>5</td>
<td>65.46</td>
<td>31.70</td>
</tr>
<tr>
<td>8</td>
<td>c</td>
<td>PVA</td>
<td>0.5</td>
<td>0.5</td>
<td>64.60</td>
<td>0.13</td>
</tr>
<tr>
<td>9</td>
<td>c</td>
<td>SDS</td>
<td>1.5</td>
<td>50</td>
<td>99.25</td>
<td>3.45</td>
</tr>
</tbody>
</table>
These results demonstrate that the organic SDS cap on the Ag particles serves as an ideal Sacrificial Passivation layer: precluding premature solid-state reaction between Ag and Sn in the powder mix, even at high temperature. The passivation however allows for the subsequent liquid phase reaction to proceed uninhibited and under further heating.

For the Cu-Sn compact in the first DSC run, the base line yielded 40 wt.% consumption of the initial Sn available. For the powder mix with PVP and SDS encapsulated particles 12 wt.% and 7 wt.% consumption respectively was achieved, suggesting a low extent of the solid-state reaction. For the second DSC run, for the baseline and for all encapsulated particles mixes similar level of the endothermic reaction was detected (around $30\% \Delta H_{Sn}$). This result indicated the amount of Sn available for liquid interaction upon further heating.

The previous findings demonstrate that the organic encapsulation with PVP and SDS of Cu particles does not serve as an ideal Sacrificial Passivation layer and does not offer the control mechanism searched for the rapid intermetallic formation approach in Cu-Sn. During undisturbed reactive diffusion the growth rate of the IMCs between Cu/Sn and Ag/Sn match a parabolic rate law [11-15] with kinetics following Arrhenius relations for the interface evolution.

Fig. 7.15  - Normalized heat of fusion of Sn based on DSC scans for chosen Cu-Sn.

A continuous and uniform IMC layer formed at the interface assures good metallurgical bond. The intermetallic reaction occurs in three consecutive stages starting from dissolution, followed by single or multiple chemical reactions and solidification. The importance of each of these stages varies between the material
systems and depends on the solubility of the “conductor metal” (like Cu, Ag or Au) in Sn. After dissolution of Cu (or Ag) in molten Sn, solid IMC begins to form at the interface [11][14][15]. This process is thermodynamically governed by the local equilibrium solubility. The conditions of this local equilibrium change locally, resulting in the consumption of one or several of the components. The difference in the passivation behaviour between Cu-Sn and Ag-Sn is driven by both the kinetics of the dissolution reaction and the general thermodynamics of the material system. The solid state reaction in Ag-Sn produces Ag₃Sn already at room temperature. The diffusion of the Ag through an interstitial mechanism in the liquid Sn is faster than self-diffusion of Sn. This reaction results in a thin layer of the IMC. In Cu-Sn system the interstitial diffusion of Cu into the liquid Sn leads to the scallop-type interface (“liquid grooving”) that originates in a requirement of the energy balance at the grain boundary [16]. The rate of gain of the Gibbs free energy is much faster in the scallop-type growth when compared to the layer type growth [11-15]. The interaction between Cu or Ag with Sn differs therefore in the nature. The rate of the free energy change favours the scallop-type IMC growth and the morphology of these Cu-Sn scallops has enabled the overall process to proceed much faster and less controllable by Sacrificial Passivation than Ag-Sn IMC layer.

The study on the sintering nature of passivated fine powders mixed with Sn (architecture of the bonding interlayer) has shown the complexity of influence parameters on the system response. The variation of response originates from the powder synthesis factors – reduction and capping agents, molar ratio and addition rate, as well as the composition and sizing of the bonding interlayer (mixture of Cu or Ag powders with Sn). The ability to tailor the thermal response of Sacrificial Passivation was proven for Ag-Sn system.

The joining experiments were followed up on with the most successful sacrificially passivated Ag/SDS-Sn powder mix.
7.5 Rapid interconnect formation using sacrificially passivated Ag-Sn powder mix

The study on the sintering nature of passivated powder mixed with Sn provided a successful control mechanism for Ag-Sn system. The best candidate encapsulation was used for the initial joining trials. To adapt the concept of hindering solid-state interaction to a joining process, Ag particles with SDS encapsulation (trail 9) were mixed with 27 wt.% Sn powder to form compacts (as shown in Fig. 7.13).

The mechanism behind is that Sn in the compact melts and spreads in the powder compact due to capillary forces. This change in the volume will re-arrange the base metal powder particles and lead to an extensive shrinkage of the compact. The samples with Sacrificial Passivation were melted in the air at 250 °C for 5 and 10 min. The trials empirically conclude that a successful passivation preventing intimate contact between the particles does not support joining process (Fig. 7.16). The decomposition of Sacrificial Passivation prevents wetting on the substrate and organic residues collect over the samples upon homogenisation of the composition.

Conclusion

The method of Sacrificial Passivation was chosen as a route to preclude solid-state interdiffusion yet allowing the subsequent liquid phase reaction to proceed uninhibited. The assembly of the alloy constituents as encapsulated metal particles was performed to achieve the consequential reduction in the relevant diffusional length scale. The successful formulation of the temporary barrier coating
was achieved for Cu and Ag particles and the thermally driven deactivation of the barrier was proven for both Cu and Ag particles. The effect of Sacrificial Passivation on solid-state reaction was quantified and the values indicated that the reaction in Ag-Sn powder mix is tuneable. The highest level of response was observed for powder mix with Ag/SDS particles. For Cu-Sn powder mix, the results were more modest. Sacrificial Passivation initially passives the base material, however the mass transport is not hindered. This behaviour was also confirmed with the characterisation of the Sacrificial Passivation in terms of reaction kinetics in the diffusion couples. The solid-state reactive interdiffusion was limited for Ag-Sn diffusion couple, but continued for Cu-Sn. Despite the desired tailoring of the thermal responses of the Sacrificial Passivation, the hindering of the solid-state diffusion as the method of controlling diffusion for rapid formation of interconnect in Cu-Sn did not yield the expected result. For the Cu-Sn system the approach of the exploitation of solid-state diffusion was then evaluated.
Bibliography

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[10]. K.K.Sobol-Sosnowska, B.A. Manhat, R. Spolenak, J. Janczak-Rusch, Science and Technology of Advanced Materials (to be submitted), "Tailoring high temperature behaviour of Ag an Cu nanoparticles by polymer encapsulation"
Chapter 8. Exploitation of solid-state interdiffusion in Cu/Sn thin films

The control of diffusion was approached in several ways over the course of this work [9]. The previous chapter dealt with a temporary kinetic barrier scenario that was proven successful for Ag-Sn binary (described in Chapter 7), but not for the Cu-Sn. In this chapter the exploitation of solid-state diffusion in Cu/Sn nano-multilayers is described. The following subchapters present results obtained and a discussion thereof. They involve a study of diffusion kinetics in Cu/Sn thin film diffusion couples with identification of dominant diffusion species for a reference to the macro-scale behaviour; identification and evaluation of the size effects in phase formation in Cu/Sn nano-multilayers at room temperature for different layer thickness regimes and molar ratios; thermal redistribution of phases was studied and approached with thermodynamic assessment. Additionally, general quality assessment of Cu/Sn samples produced by deposition methods was performed.

8.1. Quality assessment of vapour deposited samples

The metallic thin films were produced by means of the physical vapour deposition as described in the Chapter 4. The morphologies of sputtered and evaporated single layers of Cu and Sn as well as Cu/Sn multilayers at defined conditions yielded similar results. The major effect on the topography of the Sn film has its thickness, as demonstrated in Fig. 8.1. The films thicker than 50 nm were macroscopically matt grey. Whereas, the thinner Sn coatings were glossy grey, irrespective of the deposition technique used. The thicker the layer the stronger differences in roughness of the film were observed. This behaviour is reasoned in the film growth mechanisms. The Sn grows on the substrate through islanding as the primary growth mechanism. Fig. 8.2 shows the of in-plane morphology of the Cu coating produced by e-beam evaporation. The roughness of the coating changes with the film thickness. Macroscopically, the coating stays glossy irrespective of its thickness or the architecture with Sn films.
8.2. Dominate diffusive species in Cu/Sn thin bi-layer

The diffusion mechanisms present in Cu/Sn system, already at the bulk level, still raise scientific disputes, what has been discussed in the Part 1. In this subchapter, the dominating diffusion species in the Cu/Sn thin film diffusion couple (bi-layer) experiments are identified. The obtained results serve as the baseline
for the phase transformation analysis in Cu/Sn nano-multilayer architecture described in the later sections.

The thin film geometry offers additional factors. In thin films or nano-materials in general, the typical regimes for the mass transfer could differ from the bulk behaviour [1][3][19]. For this study, dominating diffusive species were evaluated in simplified bi-layer thin film diffusion couple configuration. The inert ultra-thin film of W marker was implemented in the Cu/Sn bi-layer to analyse diffusion kinetics. The W shows no known interactions with Cu and Sn\(^1\) and as an ultra-thin, discontinuous film of 1-2 nm in thickness. Additionally, it is stated W wires and films were previously successfully applied as inert markers for the system [3]. The principle of the inert marker in the diffusion couple is that the marker stays at its initial position, what allows verifying the location of Cu or Sn atoms after time and/or temperature exposure. Fig. 8.3 illustrates this principle.

Fig. 8.3 – Schematic visualisation of thin film diffusion couple with a marker, at t=0 s, and interdiffused after certain time (or temperature).

Depending on the diffusivity of the elements, the IMC or at least the presence of the other species is recorded at the preferred location in respect to the marker position.

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\(^1\) The phase diagram of Cu-W shows solubility close to 0 %, the Sn-W has not been established [2].
8.2.1. Morphology of the Cu/Sn thin film diffusion couple

A bi-layer Cu/Sn sample was prepared by means of physical vapour deposition without breaking vacuum and analysed using Rutherford Backscatter Spectroscopy, electron microscopy and X-ray diffraction for phase identification. The 560 nm Cu /200 nm Sn was deposited on Si with SiOx/SiNx diffusion barrier with a 1-2 nm thick non-uniform W marker in-between Cu and Sn film. Fig. 8.5 shows the morphology of as-deposited sample. The polycrystalline structure of the film is seen, the film is non-uniform, resembling the interconnected network of channels, resulting in a high roughness of the film ranging up to the thickness of the Sn layer itself.

The marker experiment in form of isothermal aging at the room temperature over a period of over 1500 h (2 months) was performed. The reaction between thin
films of Cu and Sn has been observed. Structural change of the Cu/Sn bi-layer as a function of annealing due to interdiffusion and reaction was investigated. The columnar structure of the Cu/Sn bi-layer merged together during isothermal aging (Fig. 8.6). The structure ages as the diffusion between the columnar grains proceeds and the surface trenches close.

Fig. 8.6 – SEM plain view of morphologies of (a) as-deposited and (b) after 1500 h at room temperature; SE, 15 kV.

The plain view morphology of the bi-layer with the aging at the 150 °C after 0.5 and 1.5 h is given in Fig. 8.7. It shows that longer annealing time leads to the formation of fine precipitates on the surface. These are not oxidation products, since the AES analysis did not confirm presence of oxygen above the solubility limits. It is therefore plausible that the IMC precipitates are observed.
8.2.2. Phase identification in Cu/Sn thin film diffusion couple

Phase identification of the Cu/Sn bi-layer structure was done using grazing incident XRD. Fig. 8.9 shows a diffraction pattern of the as-deposited and annealed at 350 °C sample. The chosen temperature of 350 °C was identified in the course of this work as the maximal process temperature for Transient Liquid Phase bonding in Cu/Sn bulk system (Chapter 6).

Fig. 8.9 – Diffractograms of 560 nm Cu /200 nm Sn in the as-deposited and post-annealed (350 °C) state: GI-XRD, theta-2theta (20-80°).
In as-deposited state, the reflections of pure Cu and Sn are clearly seen, the reflections of Cu$_6$Sn$_5$ are also present. The reflections from as-annealed at 350 °C state do not show pure Sn, yet Cu is still present. The Cu$_6$Sn$_5$ reflections are enhanced and possible growth of Cu$_3$Sn can be seen with the observation of broadening of the main Cu$_6$Sn$_5$ and Cu peaks. The reflections from SnO$_2$ were observed in the annealed sample stating Sn oxidises during annealing. The findings are in agreement with the literature. The typical phase formation during soldering involves formation of Cu$_6$Sn$_5$ at the initial solid-solid interface of Cu/Sn. With heating above 250 °C, the Cu$_3$Sn forms at the Cu/Cu$_6$Sn$_5$ interface [4][5][6]. According to the binary phase diagram of Cu-Sn the phase Cu$_6$Sn$_5$ undergoes a phase transition of ordering around 170 °C. The performed analysis, however, does not allow for the distinction between the high and low temperature variants of Cu$_6$Sn$_5$ due to the certain amount of noise left in the data given by the sample geometry.

8.2.3. Reaction kinetics of solid-solid interaction in Cu/Sn thin film diffusion couple

The kinetics in solid-solid diffusion was analysed in the Cu/Sn thin film diffusion couple by means of Rutherford Backscattered Spectroscopy (RBS) and electron microscopy enhanced with chemical analysis. The dominating diffusion species were characterized and the results were used as the baseline for the analysis of the nano-multilayer reactions.

The RBS spectrum of the as-deposited sample is shown in Fig. 8.10. The spectrum is a superposition of the spectra coming from each of the element and layer present in the sample. The location of the peaks is associated with the backscattered energy of each of the elements. The height of the peak (in respect to the ion penetration thickness) indicates the relative volume of the element present. The width indicated occurrence of the interdiffusion. The exact geometry and composition is obtained through the comparison of the data to the simulated model, as 535 nm Cu/1.5 nm W/160 nm Sn from the substrate side. The indicated regions in Fig. 8.10 (a) are W – 1; region of Sn – 2; region of Cu – 3; and a substrate – 4. Fig. 8.10 (b) shows the measurement at lower energy and indicates the W and Cu in the region – 1; Sn in region – 2; the initial interaction Cu-Sn is seen by region – 3, possible caused by the interaction with the ion beam.
Fig. 8.10 – RBS spectra of as-deposited Cu/W/Sn (535 nm Cu/1.5 nm W/160 nm Sn) thin film diffusion couple (a) at 5 MeV and (b) at 2 MeV. Region 1 – W, 2 – Sn, 3 – Cu, 4 – substrate.

Fig. 8.11 (a) shows the measured and simulated data on the sample geometry after 1500 h of isothermal aging at room temperature. The indicated regions suggest the fractional visibility of W – 1; region of pure Cu – 2; strongly interdiffused region of Cu-Sn – 3. From the analysis with the simulation tool the geometry of the sample is confirmed to 480 nm Cu/1.2 nm W/140 nm IMC from the substrate side. This Cu enriched Sn from the composition ratio modelled suggests this compound to be Cu₆Sn₅. A smeared shoulder of the Cu peak would indicate also the small amount of Sn diffusing into the Cu over the W marker forming the IMC. In fact, this behaviour is consistent with the literature observations [3]. This effect of W signal occurring also at the surface is explained by the roughness of the as-deposited Sn layer (and based on that IMC formed), what unfortunately causes reduced thickness at certain locations and exposure of W marker, what is indicated in the energy shift of the W peak location. A cross-sectional view Fig. 8.12 gives indications of W exposure. The effect is however exaggerated by a certain damage introduced during cross-sectional preparation. The pure Sn is being etched away during encapsulation of sample with FIB, due to the very high sputter rates of Sn, what was discussed in Chapter 4.
The chemical analysis at the cross-section seen in Fig. 8.12 indicates the position of the W marker and the zone around the marker with the Sn-Cu mixture phase present. The dissolution of Cu in Sn through the W marker is clearly seen. The Cu₆Sn₅ was measured at the initial Sn position and Cu₃Sn behind the marker in the direction Cu. If the diffusion fluxes of Cu and Sn were identical, the marker should be positioned in the middle of the IMC layer. Since that is not the case, the Cu atom flux must be higher than the one of Sn. Moreover, the formation of Kirkendall voids (seen in Fig. 8.12 (a)) proves a vacancy flux transport of Cu through the interface [16], making it the main diffusing species. Nevertheless, Sn diffusion occurs, but at much lower rates, causing crystalline IMC formation in Cu layer. Fig. 8.13 provides an overview of the sample microstructure. The presence of the (re-)crystallized Cu grains in the Cu layer, clearly seen in the dark field image was not expected in the non-heated sample and is probably caused by heat induced in the sample by the milling process during sample preparation. Influence of heat would also explain the presence of Cu₃Sn.
Although, thermodynamically stable from room temperature, the solid-state reaction between Cu and Sn that forms the Cu$_6$Sn$_5$ and Cu$_3$Sn is sequential regardless whether in bulk or in thin film samples. The nucleation of Cu$_3$Sn is kinetically hindered until 60 °C [3][8].
To summarise, the analysis of the bi-layered samples confirms the literature data on the phase formation behaviour of Cu-Sn. The marker experiment indicates the dominant diffusing species in IMC formation being Cu, with a limited diffusion of Sn into Cu over the W marker. The W marker is stable, reacting neither with Cu nor with Sn. The result is later used for as the reference to the bulk behaviour in the nano-multilayer approach.
8.3. Intermetallic compound formation in Cu/Sn nano-multilayers

The following chapter describes the phase formation behaviour in Cu/Sn nano-multilayers. The nano-multilayer design of the filler material was investigated for Cu/Sn alternating layers. The multilayer assured a practical advantage over single layers. In the thin film multilayer short diffusion distances are kept and enough volume to accommodate metallurgical bonding is assured.

The Cu/Sn ratios and thickness ranges of the alternating layers were selected. The various ratios were applied to evaluate its significance on the initial phase formation phenomena, the different thickness ranges were used to investigate the size effects in this formation and the identification of the energetic aspects responsible for the behaviour. The occurring solid-state interactions were characterised by means of X-ray diffraction (in grazing incident geometry (GI-XRD), Rutherford backscattered spectroscopy (RBS), and microscopy SEM/EDX and TEM/EDS. The morphology was evaluated by atomic force microscopy. Additionally, auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to support the analysis.

8.3.1. Morphology of Cu/Sn nano-multilayers

The nano-multilayered samples of Cu/Sn were deposited on the Si substrate with the SiOx/SiNx barrier coating by means of physical vapour deposition without breaking vacuum and analysed using GI-XRD, RBS, and electron microscopy. The different volume ratios of Cu:Sn and thickness of single Cu and Sn layers were used to evaluate the effect on the redistribution of phases in the nano-multilayer geometry. The list of the samples is given in Tab. 8.1. For the XRD evaluation repetition of 10 times of the bi-layer was used.

Tab. 8.1. – Description of Cu·Sn nano-multilayers samples investigated in terms of Cu/Sn ratio and Cu·Sn bi-layer thickness regime

<table>
<thead>
<tr>
<th>ratio</th>
<th>thickness of the bi-layer (aCu·bSn)x10, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>(9Cu·3Sn)</td>
</tr>
<tr>
<td></td>
<td>(30Cu·10Sn)</td>
</tr>
<tr>
<td>3:2</td>
<td>(9Cu·6Sn)</td>
</tr>
<tr>
<td></td>
<td>(30Cu·20Sn)</td>
</tr>
<tr>
<td>3:2.5</td>
<td>(6Cu·5Sn)</td>
</tr>
<tr>
<td></td>
<td>(60Cu·50Sn)</td>
</tr>
</tbody>
</table>
A typical topography of as-deposited sample is given in Fig. 8.14. It shows a rough surface with columnar growing grains. The change in the grain sizes for the nano-multilayers with initial thinner and thicker Cu/Sn bi-layers of the same ratio.

Fig. 8.14 – Topography images of 3:2 ratio nanomultilayers (a) 9 nm Cu – 6 nm Sn and (b) 30 nm Cu – 20 nm Sn; AFM tapping, (5 μm x 5 μm) and (1 μm x 1 μm).

Fig. 8.15 – STEM cross-section view of the as-deposited nano-multilayer 9 nm Cu – 6 nm Sn with EDS map (colour coding Sn – blue, Cu – red).
Fig. 8.16 – TEM cross-section view of nano-multilayer 9 nm Cu – 6 nm Sn after the in-situ HT-XRD thermal exposure at maximum of 450 °C with an EDS map (colour coding Sn – green, Cu – red, substrate – blue).
The cross-sections of (9 nm Cu – 6 nm Sn) x10 represent the sample geometry of the thinner multi-layers. The cross-section of as-deposited state was evaluated with SEM. Initially, the sample shows a multi-layered nature (Fig. 8.15). The further from the substrate, the less flat are the interfaces between the layers. The interdiffusion between the layers in as-deposited state cannot be excluded, however layers of pronounced Cu or Sn character were observed. In the annealed sample (Fig. 8.16), the grains are uniform in size of 30-60 nm, with the expected overall film thickness of around 150 nm. The EDX analysis indicates the overall presence of Sn and Cu, with certain more Cu rich regions. Typical topographies of the thicker nano-multilayers in as-deposited and after annealing state are given Fig. 8.17 for (30 nm Cu – 20 nm Sn) x10.

Fig. 8.17 – SEM plain view of (a) as-deposited (b) after the in-situ HT-XRD thermal exposure at maximum of 450 °C, nano-multilayer (30 nm Cu – 20 nm Sn) x10; SE, 20 kV.

Fig. 8.18 shows the plain view of the (60 nm Cu – 50 nm Sn) sample’s morphology in as-deposited state and after the oxidation when heated up to 800 °C.

Fig. 8.18 – SEM plain view of (a) as-deposited (b) after the in-situ HT-XRD thermal exposure at maximum of 800 °C, nano-multilayer (60 nm Cu – 50 nm Sn) x10; SE, 20 kV.

The cross-section given in Fig. 8.19 shows the microstructure of (30 nm Cu – 20 nm Sn) x10. A multi-layered nature is not clearly present, however partially lay-
ered form of Cu is maintained. The IMC grains are uniform and fine, in sizes not exceeding 50 nm. The overall film thickness is around 450 nm. The EDX analysis indicates the overall presence of Sn and Cu, with certain more Cu rich regions.

Fig. 8.19 – Cross-section of nano-multilayer (30 nm Cu – 20 nm Sn) x10; TEM, BF, DF, and EDS mapping at 200 kV (colour coding Sn – red, Cu – green).

With RBS analysis (Fig. 8.20 (a)), the interdiffusion of Cu and Sn layers in as-deposited state is clearly indicated for the thinner samples. The overall thickness for (9 nm Cu – 6 nm Sn) x10 is given as 162 nm, but the initial layers are not resolved for 10 repetitions. Nevertheless the interface position can be tracked and interlayers of Sn – 1 and Cu – 2, substrate – 3. Clearly, the Cu layer at the interface is less reacted (arrow). The singular peaks are showing the initial layers. The peaks however are smeared, most likely due to the roughness or interdiffusion occurring at the interface contact.
For the RBS analysis of thicker samples the x3 repetition of Cu/Sn bi-layer was prepared. With analysis right after the deposition the initial layered structure is indicated by the separation of the peaks for (30 nm Cu – 20 nm Sn) x3 (Fig. 8.21). The peaks are sharper for the thickener layers of Cu and Sn and no clear sign of interdiffusion is seen. The Sn layers are seen by their spectra in the region – 1, the spectra of Cu are in the region – 2. The roughness of the interfaces makes the modelling of the exact geometry impossible.

![RBS spectrum of nano-multilayer (30 nm Cu – 20 nm Sn) x3: at 2 MeV and 0° incident beam.](image)
8.3.2. Phase identification in Cu/Sn nano-multilayers by in-situ heating Grazing Incident XRD

Phase identification was performed during in-situ heating with XRD in grazing incident setup. The experimental results and the corresponding phases in the expected temperature and composition range between 30 and 300 °C are summarized in Tables 8.2-8.7. Partial matching of detected and expected equilibrium (macro) phases takes place only at the largest thickness range of the Cu-Sn. Above 300 °C primary reactions observed were oxidations of Sn into SnO₂ and Cu into Cu₂O. The oxidation reaction is tracked back to the high temperature behaviour of the XRD chamber. The chamber is evacuated using a high-vacuum pump and the measurement carried out under Ar/N₂. Nevertheless, especially at elevated temperatures, a partial N₂/O₂ exchange takes place through the X-ray windows of the chamber. Therefore the total exclusion of oxygen cannot be realized and oxygen traces cannot be completely avoided in the measuring environment. In as-deposited state, there is no clear evidence of oxide state, meaning that if the oxygen is present in the system, the amount does not exceed the solubility state [10]. The evaluation of the oxidation reactions is beyond the scope of the study, thus the transformations between 300 and 450 °C that involved oxygen interaction are not included in the phase formation analysis. Despite the observations are mentioned.

Cu:Sn ratio 3:1

✓ 9 nm Cu – 3 nm Sn

In-situ high-temperature XRD patterns are shown in Fig. 8.22. No elemental Cu or Sn peak was seen. The results of the phase composition indicate strong oxidation (SnO₂) already at room temperature. With the presence of SnO₂ the intermetallic phases are difficult to evaluate. There is an indication (single peaks) that the IMC composition could interpret as a cubic phase of the Cu₄₁Sn₁₁ with indications of orthogonal Cu₃Sn. This composition was stable up to 190 °C. During further heating, Cu₄₁Sn₁₁ transforms into hexagonal Cu₁₀Sn₃ at 200 °C. This stays stable with the continuous heating up to 300 °C, along with SnO₂.
Further heating shows oxidation, leaving the composition of Cu$_2$O and SnO$_2$ confirmed upon cooling.

The data show the sample must have had experienced significant heating either already in the production or prior measurement during setup, since two IMC phases are present at the room temperature scan, what is against the kinetic barriers known for thin film reactive diffusion, unless the room temperature is enough for the composition to undergo isothermal annealing. The presence of SnO$_2$ already at this temperature scans also indicates the exposure of the sample to the heat. These results are included for the comparison view, are not however treated quantitatively. The summary of phases is seen in the Tab. 8.2.

Tab. 8.2. – Phase occurring in the range of 30-300 °C for (9 nm Cu·3 nm Sn) x10. 3:1 ratio at xSn = 0.127.

<table>
<thead>
<tr>
<th>Temperature range T, °C</th>
<th>Phases found</th>
<th>Phases in macro phase diagram</th>
<th>Matching</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-190</td>
<td>Cu$<em>{41}$Sn$</em>{11}$ + Cu$_3$Sn (with SnO$_2$)</td>
<td>Cu$_3$Sn +Cu</td>
<td>no</td>
</tr>
<tr>
<td>200-300</td>
<td>Cu$_{10}$Sn$_3$ + Cu$_3$Sn (with SnO$_2$)</td>
<td>Cu$_3$Sn +Cu</td>
<td>no</td>
</tr>
</tbody>
</table>
In-situ high-temperature X-ray diffractograms are summarised in Fig. 8.23. A 2D multiplot from these patterns visualises the position, width and intensity change of the main peaks (Fig. 8.24). Single IMC transformation was observed during the heating up to 300 °C. The data analysis revealed at room temperature a hexagonal CuSn and a small amount of the cubic Cu. No changes were observed until 150 °C, when the transformation of Cu into orthorhombic Cu₃Sn is seen. These two phases stay stable until 300 °C.

Fig. 8.23 – Set of chosen normalised diffractograms at 30-300 °C for (30 nm Cu-10 nm Sn) x10; GI-XRD, theta-2theta (20-80°).

Fig. 8.24 – Thermodiffractogram of peak position and intensity in the (a) investigated (b) zoomed 2theta and temperature range for (30 nm Cu-10 nm Sn) x10.

The HT-XRD evaluation of the sample was continued up to 600 °C despite massive oxidation occurring in the chamber. Above 300 °C the CuSn phase disappears, leaving Cu₃Sn a single IMC until 450 °C. Aside oxidation that affects the
mass balance, from 450 °C, the Cu$_{10}$Sn$_3$ starts to appear. This phase composition stays until 600 °C.

![Phase Diagram](image)

The peaks get sharper with the increased temperature most likely due to evolution of crystallite size and homogenisation of the composition, as well as the reduction of microstrains. The main peak shifts its location and intensity due to the phase transformation. The slight shifts up to 100 °C and above 250 °C are most likely related to temperature factors. Tab. 8.3 shows obtained phase information and shows no matching with the bulk behaviour.

Tab. 8.3. – Phase occurring in the range of 30-300 °C for (30 nm Cu-10 nm Sn) x10. 3:1 ratio at xSn = 0.127.

<table>
<thead>
<tr>
<th>Temperature range T, °C</th>
<th>Phases found</th>
<th>Phases in macro phase diagram</th>
<th>Matching</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-140</td>
<td>CuSn + Cu</td>
<td>Cu$_3$Sn +Cu</td>
<td>no</td>
</tr>
<tr>
<td>150-300</td>
<td>CuSn + Cu$_3$Sn</td>
<td>Cu$_3$Sn +Cu</td>
<td>no</td>
</tr>
</tbody>
</table>

Fig. 8.25 provides correlations between the samples of the 3:1 ratio, but different thickness regimes (below and above 20 nm of the Cu-Sn bi-layer thickness) and bulk data. It is clearly given the phases formation differs for the thickness regimes. The characterized phases do not follow equilibrium phase diagram.
Fig. 8.25 – Comparison of the phases present between room temperature and 300 °C vs. equilibrium phases for the Cu-Sn nano-multilayers with bi-layers in thickness of 3:1 ratio.

**Cu:Sn ratio 3:2**

- 9 nm Cu – 6 nm Sn

In-situ high-temperature XRD patterns are shown in Fig. 8.26. The data indicate the phase composition of the sample at room temperature as cubic phase of the Cu₄₁Sn₁₁ with the leftover Cu. No Sn peak is seen, suggesting all Sn was already consumed into an IMC. During the heating, following two phase transformations were observed. Up to 110 °C there are no changes in the system. At 120 °C a new orthorhombic phase of Cu₃Sn appears along the Cu₄₁Sn₁₁ staying stable until 190 °C. With the continuous heating this phase decreases and Cu₄₁Sn₁₁ disappears, as the hexagonal phase of Cu₁₀Sn₃ grows intensively, becoming a single phase at 280 °C. The phase transformations can be shown as following:

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Phase 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>120 °C</td>
<td>200 °C</td>
<td>280 °C</td>
</tr>
<tr>
<td>δ-Cu₄₁Sn₁₁</td>
<td>δ-Cu₄₁Sn₁₁</td>
<td>ε-Cu₃Sn</td>
<td>ζ-Cu₁₀Sn₃</td>
</tr>
</tbody>
</table>

Additional heating up to 450 °C results in formation of CuO₂ and SnO₂ out of the composition, what was also confirmed with the post-annealing scan.
The peaks at room temperature are much broader due to the small grain sizes. The shape evolves with the temperature along the homogenisation of the composition and reduction of microstrains. The main peak shifts its location and intensity due to the phase transformation and possibly macrostresses release during heating. A 2D multiplot from these diffractograms visualises the position and intensity change of the main peaks (Fig. 8.27). The peaks get sharper with the increased temperature with the evolution of the grain size. Upon heating the reaction diffusion proceeds and the phase transformation is seen causing shift in the peak position.

![Graph showing diffractograms](image)

Fig. 8.26 – Set of chosen normalised diffractograms at 30-300 °C for (9 nm Cu·6 nm Sn) x10; GI-XRD, theta-2theta (20-80°).

![Graph showing thermodiffractogram](image)

Fig. 8.27 – Thermodiffractogram of peak position and intensity in the (a) investigated (b) zoomed 2Theta and temperature range for (9 nm Cu·6 nm Sn) x10.

Tab. 8.4 summarises the results observed and shows the correlation with the equilibrium phase diagram.
Tab. 8.4. – Phase occurring in the range of 30-300 °C for (9 nm Cu·6 nm Sn) x10. 3:2 ratio at xSn = 0.226.

<table>
<thead>
<tr>
<th>Temperature range T, °C</th>
<th>Phases found</th>
<th>Phases in macro phase diagram</th>
<th>Matching</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-130</td>
<td>Cu_{41}Sn_{11}</td>
<td>Cu_{3}Sn +Cu</td>
<td>no</td>
</tr>
<tr>
<td>130 - 260</td>
<td>Cu_{3}Sn</td>
<td>Cu_{3}Sn +Cu</td>
<td>no</td>
</tr>
<tr>
<td>260-300</td>
<td>Cu_{3}Sn, Cu_{10}Sn_{3}</td>
<td>Cu_{3}Sn +Cu</td>
<td>no</td>
</tr>
</tbody>
</table>

✓ 30 nm Cu – 20 nm Sn

In-situ high-temperature X-ray patterns are summarised in Fig. 8.28. The phase transformation was observed during the heating up to 300 °C. The phase composition at room temperature was characterised as the hexagonal CuSn with a small amount of the cubic Cu. No further changes were observed until 150 °C, where the transformation of Cu into orthorhombic Cu_{3}Sn was seen. These two phases stayed stable until 300 °C.

Fig. 8.28 – Set of chosen normalised diffractograms at 30-300 °C for (30 nm Cu·20 nm Sn) x10; GI-XRD, theta-2theta (20-80°).
Tab. 8.5. – Phase occurring in the range of 30-300 °C for (30 nm Cu·20 nm Sn) x10. 3:2 ratio at xSn = 0.226.

<table>
<thead>
<tr>
<th>Temperature range T, °C</th>
<th>Phases found</th>
<th>Phases in macro phase diagram</th>
<th>Matching</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-140</td>
<td>CuSn + Cu</td>
<td>Cu₃Sn +Cu</td>
<td>no</td>
</tr>
<tr>
<td>50-300</td>
<td>CuSn + Cu₃Sn</td>
<td>Cu₃Sn +Cu</td>
<td>no</td>
</tr>
</tbody>
</table>

Fig. 8.29 correlates the results of phase identification for the samples of the same ratio equal 3:2, but different thickness regimes (below and above 20 nm of the Cu·Sn bi-layer thickness). The results are compared against bulk information. Similarly to the 3:1 ratio samples, the phase formation differs for the thickness regimes and do not follow equilibrium phase diagram.

**Cu:Sn ratio 3:2.5**

![In-situ high-temperature XRD patterns](image)

In-situ high-temperature XRD patterns are shown in Fig. 8.30. The phase at room temperature is identified as cubic phase of the Cu₄₁Sn₁₁ with a certain
amount of pure Cu. Not even at this high Sn content the unbound Sn was seen. The whole volume of Sn is transformed into IMC. Up to 100 °C there are no changes in the system. At 110 °C the orthorhombic Cu$_3$Sn appears aside Cu$_{41}$Sn$_{11}$. The Cu$_3$Sn peaks grow until 180 °C, where Cu$_{41}$Sn$_{11}$ transforms into a hexagonal Cu$_{10}$Sn$_3$. The new phase grows intensively, becoming a single phase at 280 °C. The following heating up to 450 °C results in oxidation of the components into CuO$_2$ and SnO$_2$, what was also confirmed with the post-annealing scan.

Fig. 8.30 – (a) Set of chosen normalised diffractograms at 30-300 °C for (6 nm Cu·5 nm Sn) x10; GI-XRD, theta-2theta (20-80°).

A 2D multiplot made from these diffractograms visualises the position and intensity change of the main peaks (Fig. 8.31).

Fig. 8.31 – Thermodiffractogram of peak position and intensity in the (a) investigated (b) zoomed 2Theta and temperature range for (6 nm Cu·5 nm Sn) x10.

The peaks at room temperature are much broader most likely due to the inhomogeneities, small grain sizes and microstrains present in the sample. The shape evolves with the temperature along the homogenisation of the composition and
reduction of microstrains. The main peak shifts its location and intensity due to the phase transformation.

The phase transformations can be shown as following:

Tab. 8.6 summarises the results observed and shows the correlation with the equilibrium phase diagram.

Tab. 8.6. – Phase occurring in the range of 30-300 °C for (6 nm Cu·5 nm Sn) x10. 3:2.5 ratio at $x_{Sn} = 0.268$.

<table>
<thead>
<tr>
<th>Temperature range $T$, °C</th>
<th>Phases found</th>
<th>Phases in macro phase diagram</th>
<th>Matching</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-100</td>
<td>$\delta\cdot Cu_{41}Sn_{11}$ + Cu</td>
<td>$\varepsilon\cdot Cu_{3}Sn$ +Cu</td>
<td>no</td>
</tr>
<tr>
<td>110-180</td>
<td>$\delta\cdot Cu_{41}Sn_{11}$ + $\varepsilon\cdot Cu_{3}Sn$</td>
<td>$\varepsilon\cdot Cu_{3}Sn$ +Cu</td>
<td>no</td>
</tr>
<tr>
<td>190-250</td>
<td>$\varepsilon\cdot Cu_{3}Sn$ + $\zeta\cdot Cu_{10}Sn_{3}$</td>
<td>$\varepsilon\cdot Cu_{3}Sn$ +Cu</td>
<td>no</td>
</tr>
<tr>
<td>260-300</td>
<td>$\zeta\cdot Cu_{10}Sn_{3}$</td>
<td>$\varepsilon\cdot Cu_{3}Sn$ +Cu</td>
<td>no</td>
</tr>
</tbody>
</table>

✓ 60 nm Cu – 50 nm Sn

In-situ high-temperature XRD patterns are given in Fig. 8.32 and a 2D multiplot from these diffractograms with the position and intensity change of the main peaks in Fig. 8.33. In the analysed temperature range, a single phase transformation was observed. The phase composition at room temperature is a monoclinic $Cu_{6}Sn_{5}$ with a small amount of the pure Cu. It is clearly seen, that up to 140 °C there are no changes in the system. At 150 °C the orthorhombic $Cu_{3}Sn$ appears. The phase mixture $Cu_{6}Sn_{5}$ and $Cu_{3}Sn$ stays stable up to 300 °C. A low intensity peak of Pt is seen due to the sample fixation.

These phase transformations can be schematically presented:
Similarly, the peaks get sharper with the increased temperature with the evolution of the crystallite sizes. Upon heating the reaction diffusion proceeds and the phase transformation takes place causing shift in the peak position.

Fig. 8.32 – Set of chosen normalised diffractograms at 30–300 °C for (60 nm Cu·50 nm Sn) x10; GI-XRD, theta-2theta (20–80°).

Fig. 8.33 – Thermodiffractogram of peak position and intensity in the (a) investigated (b) zoomed 2theta and temperature range for (60 nm Cu·50 nm Sn) x10.

Tab. 8.7 summarises the observations in comparison to the equilibrium bulk behaviour. The data obtained match the bulk behaviour of Cu·Sn alloys.
With matching correlation to the bulk behaviour, the sample of this composition was further heated to 800 °C. With the continuous heating the cubic phase of Cu₆Sn₅ decreases and it is almost completely gone at 400 °C, with the two new phases appearing – the hexagonal phase of Cu₁₀Sn₃ and cubic phase of Cu₄₁Sn₁₁. At the same temperature the SnO₂ peal is excessively growing. The cubic phase of Cu₄₁Sn₁₁ is completely gone at about 650 °C. On the continuous heating the hexagonal phase Cu₁₀Sn₃ disappears and Cu starts to oxidise as Cu₂O peak appears. The pattern obtained after cooling is the same as at 800 °C, the thermal expansion is observed.
Fig. 8.34 shows the comparison of phases formed in the samples of the 3:2.5 ratio, but different thickness regimes. The phases found during evaluation of the 6 nm Cu – 5 nm Sn samples differ from the equilibrium phases. However, for the 60 nm Cu – 50 nm Sn samples, the IMC formed follow the expected phases. The temperature regimes are not identical to equilibrium data, nonetheless, the strong correlation is observed. The obtained results are analysed and discussed in the later sections of this Chapter.
8.3.3. Lattice strain evaluation of as-deposited Cu/Sn nano-multilayers

The identification of phases in the multi-phase system requires consideration of the residual stress present in the system. If the residual stresses exist within the sample, then the spacing $d_{hkl}$ will be different to the unstressed state. The phase identification indicates the occurrence of the $\delta$-Cu$_{41}$Sn$_{11}$ at room temperature for Cu-Sn nano-multilayers (bi-layers below 20 nm), irrespective of the initial composition (sample Cu/Sn ratio). It was observed that the peak positions of the samples are slightly below the reference values for unstrained lattice of the bulk phases [21]. This minimal change in the peak position may indicate stress state due to reactive interdiffusion leading to volumetric changes, but also change in the local stoichiometry caused by the nucleation and growth of the IMC grains or the overall geometry of the samples. The analysis of the lattice strain in the experimental approach used is very limited, as the GI-XRD in theta-2theta configuration is not optimal for that kind of analysis in the thin film geometry [20]. The GI-XRD maintains a constant area irradiated, increasing the signal broadening for high angle diffraction peaks. The Bragg-Brentano geometry can only probe crystallite dimensions through the thickness of the film and indicates the in-plane crystallite sizes. Moreover, the in-situ heating does also affect the exact positioning and peaks. These effects cannot be excluded, nonetheless the indications of the lattice strain were evaluated for the room temperature patterns. The approach allows only for a rough estimation of the residual stresses. The analysis was done using a single peak from the 30-50° 2theta angle pattern (to exclude effects of asymmetries of the peaks below 30° and instrumental effects of peak broadening at high angles).

The stress estimation from 660 reflexes (main peak) for all compositions is given in Tab. 8.8. The out of plane strain is calculated from the difference of the measured and reference lattice spacing $d_{660} = 2.117$ Å. There are neither data on elastic constants for Cu$_{41}$Sn$_{11}$ available, nor the temperature variation of them for other Cu-Sn IMC. To estimate the relative difference in stress, the bulk reference values of room temperature elastic modulus $E$ and Poisson’s ratio $\nu$ for Cu$_6$Sn$_5$ were used ($E = 96.9$ GPa, $\nu = 0.309$ [22]).

According to these calculations compressive stresses are present in all as-deposited samples for Cu-Sn bi-layers below 20 nm. It is important to remember,
the values of these stresses are only used for the relative comparison\(^\text{2}\). The stresses increase into compressive regime with the higher content of Sn in the initial composition.

Tab. 8.8. – Measured lattice spacing at 660 reflex of Cu\(_{41}\)Sn\(_{11}\) and the stresses calculated from the deviation between strained and unstrained lattice.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position of 660 reflex, °</th>
<th>(d_{660}), Å</th>
<th>(\sigma), MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio 3:1 (9Cu-3Sn)</td>
<td>42.7</td>
<td>2.118</td>
<td>-16</td>
</tr>
<tr>
<td>Ratio 3:2 (9Cu-6Sn)</td>
<td>42.6</td>
<td>2.122</td>
<td>-157</td>
</tr>
<tr>
<td>Ratio 3:2.5 (6Cu-5Sn)</td>
<td>42.5</td>
<td>2.127</td>
<td>-314</td>
</tr>
</tbody>
</table>

This could be related to the geometrical constrains of the multilayer and deposition method. The sputtered thin films are typically under a certain amount of internal stresses (tensile or compressive) depending on material, substrate and deposition parameters. As a consequence the lattice parameters change to shorter or longer values and the diffraction peaks shift slightly. Furthermore, the measured residual stresses can be strongly influenced by the surface roughness. In multilayer systems the interfaces are imperfect due to interdiffusion and reactivity of materials what affects the X-ray reflectivity and modifies the pattern [23]. Additionally, the formation mechanisms of IMC in the Cu-Sn system could play a role. Cu has a face-centre cubic lattice and the metallic Sn exists in body centred tetragonal structure. The Cu atoms are roughly 20% smaller than the ones of Sn, allowing for a reasonable amount of space between Cu atoms, when the lattice is close packed on the Sn layer. Therefore, Cu diffuses exceptionally quickly in the interstitial sites of Sn. The concentration of stacking faults increases with the quantity of a Sn dissolved in Cu. The crystalline structure gets distorted, what could be seen by the slight asymmetric broadening and shift of an XRD peak pattern.

The major expected peaks are present with the intensity distribution is close to bulk reference. There is an average shift in the position of the peaks of 0.02 degree to lower 2theta values. Though, the reference diffraction patterns of Cu-Sn IMCs lay very close to each other (on the average 0.16 degree) and tens of low intensity peaks are present. The similarly calculated lattice strains for the Cu\(_{16}\)Sn\(_{3}\) \((d_{300} = 2.111 \text{ Å})\) stipulate much higher stress levels (as shown in Tab. 8.9) than for the Cu\(_{41}\)Sn\(_{11}\).

\(^{2}\) These calculated stresses are not absolute, since the references are not available for Cu\(_{41}\)Sn\(_{11}\) and the elastic constants for CuSn bulk phases were used. However, the elastic moduli of IMC are not expected to follow a linear superposition law of the constituent elements, due to the changes in electronic structure associated with alloying [22].
Tab. 8.9. – Calculated lattice spacing at 300 reflex of Cu10Sn3 and the stresses from the deviation between strained and unstrained lattice.

<table>
<thead>
<tr>
<th>Sample</th>
<th>d_{300}, Å</th>
<th>σ, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio 3:1 (9Cu-3Sn)</td>
<td>2.118</td>
<td>-204</td>
</tr>
<tr>
<td>Ratio 3:2 (9Cu-6Sn)</td>
<td>2.122</td>
<td>-345</td>
</tr>
<tr>
<td>Ratio 3:2.5 (6Cu-5Sn)</td>
<td>2.127</td>
<td>-502</td>
</tr>
</tbody>
</table>

Thus, results indicate the observed patterns originate for slightly strained Cu41Sn11 lattice.

The similar lattice strain evaluation for Cu·Sn nano-multilayers (30 nm Cu – 10 nm Sn) and (30 nm Cu – 20 nm Sn) yielded the average shift in the position of the peaks of 0.06 degree to higher 2theta values (with the calculated tensile stress of 94 MPa). The Cu·Sn nano-multilayers (60 nm Cu – 50 nm Sn) showed the average of 0.14 degree shift towards lower angles (and compressive stress of -188 MPa).
8.3.4. Analysis and assessment of thermodynamics of phase formation in Cu/Sn nano-multilayers based on experimental results

The experimental results and corresponding phases from the phase diagram were summarized in Tables 8.2-8.7. The results show certain discrepancy between the detected and the expected phases. At the room temperature, a first nucleated phase does not depend on the overall composition of the sample, but on the thickness of the alternating layers. The effect is particularly vivid for Cu-Sn bi-layers below 100 nm thickness. A thermodynamic assessment of Cu-Sn phase formation at room temperature for nano-multilayers has been performed and compared against experimentally obtained phase analysis.

The amount of Sn was calculated for different sample ratios and the theoretical assessment was performed. The materials balance is given by the Eq. (8.1):

\[ x_{Sn} = y_{a} \cdot x_{Sn(a)} + (1 - y_{a}) \cdot x_{Sn(\beta)} \]  \hspace{1cm} (Eq. 8.1)

where \( x_{Sn} \) is the average mole fraction of Sn in the produced alloy, \( x_{Sn(a)} \) and \( x_{Sn(\beta)} \) are the mole fractions of Sn in given phases, \( y_{a} \) is the phase ratio.

The expected molar phase ratio is reported in Tab. 8.10 and visualized in Fig. 8.35 as the expected behaviour lines. The phase ratio has been calculated by mole of atoms.

All values are in mole (atom) fractions, dimensionless. From Eq. (8.2):

\[ y_{a} = \frac{x_{Sn} - x_{Sn(\beta)}}{x_{Sn(a)} - x_{Sn(\beta)}} \]  \hspace{1cm} (Eq. 8.2)

The average mole fraction is calculated as:

\[ x_{Sn} = \frac{\delta_{Sn}}{\delta_{Sn} + \delta_{Cu}} = \frac{1}{1 + 2.28 \cdot \frac{\delta_{Cu}}{\delta_{Sn}}} \]  \hspace{1cm} (Eq. 8.3)

where \( \delta_{Sn} \) and \( \delta_{Cu} \) are the thickness of the Sn- and Cu-films, respectively (nm, or at least in the same unit), 16.2 and 7.10 are the molar volumes of pure Sn and Cu respectively at room temperature (in cm³/mol).
Fig. 8.35 – Cu-Sn phase diagram with compositions expected for the chosen Cu-Sn bi-layer ratios (3:1, 3:2, 3:2.5).

The mole fraction is a function of thicknesses ratio of the components. The mole fractions of Sn in stoichiometric compounds Cu$_6$Sn$_5$ is calculated as:

$$x_{Sn(a)} = \frac{s}{c+s} \quad (Eq. \ 8.4)$$

If the phase is not stoichiometric, the value of $x_{Sn(a)}$ can be read from the phase diagram of Fig. 8.35. The phase ratio expressed in atom-mole fraction ($y_\alpha$) can be re-calculated to the volume ratio ($\phi_\alpha$) as:

$$\phi_\alpha = \frac{y_\alpha \cdot V_\alpha}{y_\alpha \cdot V_\alpha + (1-y_\alpha) \cdot V_\beta} \quad (Eq. \ 8.5)$$

where $V_\alpha$ and $V_\beta$ are the molar volumes (cm$^3$/mol·atom) of the two phase, respectively. It can be calculated as:

$$V_\alpha = \frac{M_\alpha}{\rho_\alpha} \quad (Eq. \ 8.6)$$

where $M_\alpha$ is the average atomic mass of phase $\alpha$ (g/mol), $\rho_\alpha$ is the density of phase $\alpha$ (g/cm$^3$). The average atomic mass is calculated as (in g/mol):

$$M_\alpha = 63.546 + 55.144 \cdot x_{Sn(a)} \quad (Eq. \ 8.7)$$
Tab. 8.10. – Average molar mass, density and molar volume of Cu·Sn phases (calcula-
tion with equations (Eq. 8.4, 8.6, 8.7), density of elements from G, density of com-
pounds from J).

<table>
<thead>
<tr>
<th>Phase</th>
<th>$x_{Sn(x)}$</th>
<th>$M_x$ (g/mol)</th>
<th>$\rho_x$, g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0</td>
<td>63.55</td>
<td>8.95</td>
</tr>
<tr>
<td>Cu$\text{Sn}_{11}$</td>
<td>0.212</td>
<td>75.24</td>
<td>8.96</td>
</tr>
<tr>
<td>Cu$\text{Sn}_3$</td>
<td>0.231</td>
<td>76.28</td>
<td>9.08</td>
</tr>
<tr>
<td>Cu$\text{Sn}$</td>
<td>0.250</td>
<td>77.33</td>
<td>9.14</td>
</tr>
<tr>
<td>Cu$\text{Sn}_5$</td>
<td>0.455</td>
<td>88.64</td>
<td>8.45</td>
</tr>
<tr>
<td>Cu$\text{Sn}$</td>
<td>0.5</td>
<td>91.118</td>
<td>7.78</td>
</tr>
<tr>
<td>Sn</td>
<td>1</td>
<td>118.69</td>
<td>7.33</td>
</tr>
</tbody>
</table>

Tab. 8.10 describes thermodynamic properties of the Cu·Sn IMC. The molar vol-
ume of ideal compound was calculated as an additive value from the pure compo-
nents:

\[ V_{id} = 7.10 + 9.10 \cdot x_{Sn} \quad (\text{Eq. 8.8}) \]

The example of calculation for the ratio 3:2 in the thickness 9 nm Cu – 6 nm Sn, is given below. Other results are summarized in the Tab. 8.11.

The ideal total thickness is of each of the layers $\delta_{Sn}$ and $\delta_{Cu}$ makes an average mole fraction from Eq. (8.2): $x_{Sn} = 0.222$, with the assumption the encapsulating flash of Cu.

Fig. 8.36 provides an overview of the room temperature intermetallic compounds expected based on the sample composition and observed with the phase analysis.
With this result a case study based analysis was performed to provide understanding of the energetically aspects of the size effects.

**Case 1 – macro-equilibrium at room temperature.**

Case 1a – Equilibrium phases and compositions: \( \alpha = \text{Cu}, \ \beta = \text{Cu}_6\text{Sn}_5, \ x_{\text{Sn} (\alpha)} = 0 \)

\[ x_{\text{Sn} (\beta)} = 0.4545 \] (see Tab. 8.10).

Phase ratio from Eq. (8.2):

\[ y_{\alpha} = \frac{0.222 - 0.4545}{-0.4545} = 0.511 \]

From Eq. (8.5): \( \phi_{\alpha} = 0.607 \), the system contains 61 vol.% of Cu and 39 vol.% of Cu_6Sn_5.

Case 1b – Equilibrium phases and compositions: \( \alpha = \text{Cu}, \ \beta = \text{Cu}_3\text{Sn}, \ x_{\text{Sn} (\alpha)} = 0 \)

\[ x_{\text{Sn} (\beta)} = 0.250 \] (see Tab. 8.10).

Phase ratio from Eq. (8.2):

\[ y_{\alpha} = \frac{0.222 - 0.250}{0 - 0.250} = 0.112 \]

Thus, the system is made of 88.8 atom% of Cu_3Sn + 11.2 atom% of Cu, what makes from Eq. (8.5): \( \phi_{\alpha} = 0.0957 \). Thus, the system contains 9.57 vol.% of Cu and 90.43 vol.% of Cu_3Sn.

**Case 2 – size effect measured at room temperature.**

If the phase observed is \( \alpha = \text{Cu}_{41}\text{Sn}_{11} \). Then, \( x_{\text{Sn} (\alpha)} = 0.212 \). The value is higher than the average mole fraction of 0.222 for Cu_{41}Sn_{11}, explaining the additional phase is needed for materials balance.

Case 2a – Supposing the second phase is \( \beta = \text{Sn} \). Then, \( x_{\text{Sn} (\beta)} = 1 \) (see Tab. 8.10).

Phase ratio from Eq. (8.2):

\[ y_{\alpha} = \frac{0.222 - 1}{0.212 - 1} = 0.987 \] Thus, the system is made of 98.7 atom% of Cu_{41}Sn_{11} + 1.3 atom% of Sn. Using Eq. (8.5): \( \phi_{\alpha} = 0.975 \). Thus, the system contains 97.5 vol.% of Cu_{41}Sn_{11} and 2.5 vol.% of Sn. If this Sn is oxidized then its volume fraction would increases. This low value of 2.5 vol.% would most likely not allow to visual Sn-peak in the noisy spectrum during diffraction measurement.

Case 2b – Supposing the second phase is \( \beta = \text{Cu}_3\text{Sn} \). Then, \( x_{\text{Sn} (\beta)} = 0.25 \) (see Tab. 8.10).

Phase ratio from Eq. (8.2):

\[ y_{\alpha} = \frac{0.222 - 0.25}{0.212 - 0.25} = 0.737 \] Thus, the system is made of 73.7 atom% of Cu_{41}Sn_{11} + 26.3 atom% of Cu_3Sn. Using Eq. (8.5): \( \phi_{\alpha} = 0.736 \). Thus, the system contains 73.6 vol.% of Cu_{41}Sn_{11} and 26.4 vol.% of Cu_3Sn. This amount is detectable by the XRD measurement.
Case 2c – The observation, however suggests the second phase to be \( \beta = \text{Cu} \), 
\[ x_{\text{Sn}(\alpha)} = 0.212, \quad x_{\text{Sn}(\beta)} = 0 \] (see Tab. 8.10). Phase ratio from Eq. (8.2): 
\[ y_\alpha = \frac{0.222 - 0}{0 - 0.250} = -0.112 \] Thus, the system is made of 88.8 atom\% of \( \text{Cu}_{41}\text{Sn}_{11} \) + 11.2 atom\% of \( \text{Cu} \), what makes from Eq. (8.5): \( \phi_\alpha = 0.8966 \). Thus, the system contains 10.33 vol.\% of \( \text{Cu} \) and 89.67 vol.\% of \( \text{Cu}_{41}\text{Sn}_{11} \). This theoretical analysis was confirmed by the diffraction experiments. The XRD at room temperature gives the indications of free \( \text{Cu} \) left aside of the IMC. The cross-section view also shows unreacted layer of \( \text{Cu} \) at the substrate side.

Tab. 8.11 provides calculated results of the volume fractions for the phases found at room temperature for each of the samples used for size effect analysis based on similar case study approach.

Tab. 8.11. – Case study analysis of the found phases during XRD measurements at room temperature.

<table>
<thead>
<tr>
<th>samples</th>
<th>(9Cu-6Sn)</th>
<th>(6Cu-5Sn)</th>
<th>(30Cu-10Sn)</th>
<th>(30Cu-20Sn)</th>
<th>(60Cu-50Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>xSn</td>
<td>0.222</td>
<td>0.261</td>
<td>0.127</td>
<td>0.225</td>
<td>0.267</td>
</tr>
<tr>
<td>volume %</td>
<td>86% ( \text{Cu}<em>{41}\text{Sn}</em>{11} ) + 14% ( \text{Cu} )</td>
<td>86% ( \text{Cu}<em>{41}\text{Sn}</em>{11} ) + 14% ( \text{Cu} )</td>
<td>76% ( \text{CuSn} ) + 24% ( \text{Cu} )</td>
<td>81% ( \text{CuSn} ) + 19% ( \text{Cu} )</td>
<td>84% ( \text{Cu}_6\text{Sn}_5 ) + 16% ( \text{Cu} )</td>
</tr>
</tbody>
</table>
8.3.5. Length scale assessment and analysis for Cu/Sn nano-multilayers

Nano-multilayers with Cu/Sn bi-layer below 20 nm

All nano-multilayers samples of less than 20 nm of the Cu-Sn bi-layer show the unusual initial phase formation behaviour caused by the meta-stable state of the films. Further heating leads to homogenization, however the later phases are still not following the equilibrium bulk phase diagram either.

The comparison chart given in Fig. 8.37 provides a visual interpretation of the phases found during investigation of the samples below 20 nm of the Cu-Sn bi-layer. The findings are compared against bulk state. The phases observed and their temperature ranges of existence are fairly similar over the length scale. Based on composition expected phases are for 3:1 and 3:2 – Cu+Cu₃Sn, and for 3:2.5 – Cu₅Sn₅+Cu₃Sn, however these phases were not observed. The first occurring phase is cubic δ-Cu₄₁Sn₁₁ aside of Cu excess, no unbound Sn was found. The Cu₄₁Sn₁₁ is not expected by the composition given, neither the temperature regime. The Cu₄₁Sn₁₁ also does not occur in bulk until 350 °C. This phenomenon is unusual for Cu-Sn system at the temperature and has not been reported before. The Cu₄₁Sn₁₁ is an intermetallic phase at 32.5 wt.% Sn with an ordered gamma brass structure and a cell parameter of 17.96 Å. Macroscopically, the δ-phase is stable between 348 °C and 586 °C [11][12][13]. Metallurgically, the phase is seen upon quenching. Interestingly, it was observed in electrodeposited low Sn³ content films (annealed for 12 h at 200 °C) [14]. It was stated that the phase was stabilised by the plating procedure. Although, when discussing the factors determining the structure of the electrodeposited alloy, it is concluded that it is govern by the kinetics rather than the thermodynamics, when using surface-active substances [15].

For the equilibrium system, the initial phase growth mechanism indicates single phase formation at room temperature. It is argued that the phase formation at the Cu/Sn interface occurs per molecule not per atom, since only if the molecule is formed the full gain of energy from chemical potential is obtained [16].

The room-temperature interaction of Cu and Sn in lowest regime leads to nucleation of the Cu₄₁Sn₁₁, no other IMC phase was observed. The nucleation and side-by-side growth, of the other phases at this temperature is kinetically not favoured for the thin films. The 3:1 ratio sample shows two IMC regimes at room

---

³ the exact sample geometry and composition is not stated
temperature, indicating the sample must have experienced increased temperature before testing.

After the Cu$_{41}$Sn$_{11}$ is nucleated and homogenized, the later transformations into Cu$_3$Sn and Cu$_{10}$Sn$_3$ are observed for all the samples in spite of their Cu/Sn ratio. The differences in temperature ranges between samples of 3:2 and 3:2.5 ratios is attributed to the energy stored in the system with the oversaturation, stress state and experimental setup.

The IMC transformation path indicates initial formation of cubic lattice of a massive unit cell – Cu$_{41}$Sn$_{11}$. The initial Cu layer is strongly bound to the substrate, and its reactivity is limited in comparison to the later layers as seen in TEM cross-section. One could speculate this initial Cu film is a seeding layer for the formation of the cubic Cu$_{41}$Sn$_{11}$. With raising temperature the phase transforms into orthorhombic Cu$_3$Sn to finally precipitate with hexagonal cell of Cu$_{10}$Sn$_3$. The Cu$_{41}$Sn$_{11}$ has lower interface energy against Cu than Cu$_6$Sn$_5$ or Cu$_3$Sn. It is most likely oversaturated, since the creation of the new interface would require higher energy. The minimal Gibbs energy of formation is, however, seen for Cu$_{10}$Sn$_3$, although the difference to Cu$_{41}$Sn$_{11}$ is very small. The formation of

![Fig. 8.37 – Comparison of the phases present between room temperature and 300 °C vs. equilibrium phases for the nano-multilayers with Cu–Sn bi-layers in thickness below 20 nm.](image)

The IMC transformation path indicates initial formation of cubic lattice of a massive unit cell – Cu$_{41}$Sn$_{11}$. The initial Cu layer is strongly bound to the substrate, and its reactivity is limited in comparison to the later layers as seen in TEM cross-section. One could speculate this initial Cu film is a seeding layer for the formation of the cubic Cu$_{41}$Sn$_{11}$. With raising temperature the phase transforms into orthorhombic Cu$_3$Sn to finally precipitate with hexagonal cell of Cu$_{10}$Sn$_3$. The Cu$_{41}$Sn$_{11}$ has lower interface energy against Cu than Cu$_6$Sn$_5$ or Cu$_3$Sn. It is most likely oversaturated, since the creation of the new interface would require higher energy. The minimal Gibbs energy of formation is, however, seen for Cu$_{10}$Sn$_3$, although the difference to Cu$_{41}$Sn$_{11}$ is very small. The formation of
Cu$_{41}$Sn$_{11}$ may be determined by the specific influence of the interfaces – the component with lower surface energy diffuses faster to the surface. This is supported by the analysis of (9 nm Au – 6 nm Sn) x10 nano-multilayer, where the equilibrium phases transition paths were observed. For the Au-Sn IMCs the differences between the formation energies for different compounds are very significant, what could indicate that this extra interface energy added to the system does not play a role for that system.

The system tends to form a phase with the lowest Gibbs energy at the largest energy gain upon formation of the molecule (the literature values are reported in Chapter 2, Tab 2.4). Although, the Cu$_3$Sn phase had lower free energy has a defined equilibrium concentration, there is a local minimum that causes the nucleation of Cu$_{41}$Sn$_{11}$ phase instead. The formation of Cu$_{41}$Sn$_{11}$ can be argued to be based on Ostwald rule of stages, stating the system approaches the equilibrium state with steps involving the minimum change of the free energy rather than reaching the equilibrium state directly. The crystallization from solutions starts from thermodynamically unstable phases followed by recrystallization to thermodynamically stable ones [17]. The concentration of Sn increases in the phase to the supersaturated state to extend, where the formation of Cu$_3$Sn become favourable.

![Bulk equilibrium Cu-Sn phase diagram with the indicated high-Cu region and phases of interest.](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice</th>
<th>Tm, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ - Cu$<em>{41}$Sn$</em>{11}$</td>
<td>cubic</td>
<td>582</td>
</tr>
<tr>
<td>ε - Cu$_3$Sn</td>
<td>orthorhombic</td>
<td>676</td>
</tr>
<tr>
<td>ζ - Cu$_{10}$Sn$_3$</td>
<td>hexagonal</td>
<td>642</td>
</tr>
</tbody>
</table>

It is claimed that in order to achieve a thermodynamic stability, the system has to undergo all the transition from cooling till solidification, even at reaction temperature below that indicated by the phase diagram or in solid-state [19]. This
argues that the amount of such phases is required for the nucleation process and in a bulk material is simply not enough to be determined. That does not explain the formation behaviour at higher temperatures, where the untypical reordering takes place. More probable explanation lies in the geometrical nature of the sample – high value of interfaces and associated interfacial energy.

Nano-multilayers with Cu/Sn bi-layer above 20 nm

The comparison chart given in Fig. 8.39 provides a visual interpretation of the phases found during investigation of the sample with the Cu/Sn bi-layer above 20 nm in thickness. The findings are compared against bulk equilibrium state. The phases observed and their temperature ranges differ over the length above 20 nm bi-layer. However, the ratio does not seem to impact the phase formation. Nonetheless, a single IMC nucleation at the side of excess Cu is seen for all samples in as-deposited state. The initially nucleated phase seems to depend on the initial thickness of the layers. In that respect, length scale effect is clearly observed. For the thickness above 20 nm, but below 100 nm of the Cu/Sn bi-layer the first occurring phase is hexagonal CuSn.

Fig. 8.39 - Comparison of the phases present between room temperature and 300 °C vs equilibrium phases for the nano-multilayers with Cu-Sn bi-layers in thickness above 20 nm.
The CuSn is not a phase found in the metallurgical alloys, as it is claimed to transform rapidly into other high temperature phases. It has hexagonal unit cell with a cell parameter of 4.2 and 5.1 Å (Fig. 8.40) [18].

![Fig. 8.40 - Unit cell of CuSn](image)

It was observed in electrodeposited samples, and is believed to be an intermediate hexagonal closed packed phase that forms due to increases concentration of the stacking faults at high levels of Sn. It is reported to transform upon 3 h annealing at 350 °C ordered high-temperature hexagonal closed packed phase, which is present in the equilibrium phase diagram, i.e. $\zeta$-Cu$_{10}$Sn$_3$ [15]. In the current work Cu$_5$Sn formation is seen above 150 °C. The Cu$_{10}$Sn$_3$ has only been observed at higher temperatures. For the (60 nm Cu – 50 nm Sn) the initial phase formed is Cu$_6$Sn$_5$. At higher temperatures the sample behaves within the benchmark given for the bulk, with the formation of Cu$_3$Sn.

**Comparison of IMC phase formations in Cu/Sn nanomultilayers across the different length scales**

The findings on the size effects in the phase formation of Cu-Sn are collected in Fig. 8.41. This chart shows also data obtained for the temperature above 300 °C, despite these measurements happened under oxidation in the heating chamber of the XRD device. The strong oxidation was not seen for the thickest 60 nm Cu – 50 nm Sn sample. There is no data shown above 300 °C for regime below 20 nm Cu/Sn bi-layer. The thinnest samples oxidized completely at higher temperatures. Interestingly, the different phase behaviour schemes are observed. In those terms, the three length scale regimes can be determined that result in a different phase formation, and by that thermodynamic behaviour.

A transition length scale between “nano-phase” formation (below 20 nm in bi-layer thickness) and almost bulk-like (above 100 nm) is seen. The samples below 20 nm of the bi-layer initially form a phase of the low enthalpy of formation. The energy levels of Cu$_{41}$Sn$_{11}$, Cu$_3$Sn and Cu$_{10}$Sn$_3$ are very close to one another. The particular phase is chosen by the kinetics of the interfacial reaction. The driving
force associated with chemical potential, the chemical affiliation of Cu and Sn and the interfacial mobility makes formation of a large, semi-ordered lattice. The cubic lattice of Cu$_{41}$Sn$_{11}$ the best accommodates the rapid diffusion process occurring at such short diffusion distances. The composition is maintained by the creation of vacancies or substitution atoms rather than by taking up an interstitial position in the lattice. It is likely that the variation in composition of the intermetallic phase is accommodated by fewer Cu interstitials for the case of excess Sn and by Sn vacancies or Cu substitution on the Sn sites for the case of excess Cu.

Fig. 8.41 – Size effects in phase transformations in Cu-Sn nano-multilayers. The transition is seen for the 50 nm length scale regime. The sample shows behaviour not seen in the conventional Cu-Sn metallurgical reactions. The hexagonal CuSn phase is claimed to be unstable and thus undetectable. It has however been reported to be stabilized in electrodeposited thin films, as a result of deposition parameters and surface activation substances in the electrochemical bath. Its presence in the metallurgical thin films, suggests an interaction between the driving forces. The phase must be stabilized by the interfacial or even strain energy stored in the sample during deposition and followed interdiffusion. The transition occurs since the sample geometry imposes not only short diffusion distances, but also a large “volume” of the interfaces that affects the phase for-
mation as is the driving factor for the transformations observed between Cu and Sn.

For samples above 100 nm of the bi-layer, the phase formation occurs through (or close) the conventional reaction path. The phase formation is still very rapid; however the amount of “bulk” atom is enough for the atoms to respond in the way close to the equilibrium. The differences of the temperature regimes are, still however, associated with the interfacial energy of the system.

Conclusion

Phase formation and interdiffusion that occur in the thin layers deposited are observed to be different to that expected simply from the bulk phase diagram. The most significant change was seen in the phase formed in as-deposited state for different thicknesses, regardless of the Cu:Sn ratio, clearly stating the existence of the size-effect in the phase formation.

Particularly, for the case of fast diffusion of Sn atoms the formation of “meta-stable” phases can be observed. However, these phases are stable for a certain temperature-concentration-length scale regimes they have been observed at.

The initial diffusion leads to the formation and growth of a metastable solution with a sharp concentration profile. With temperature a new phase nucleates just by reconstruction of atomic order, without immediately changing the concentration profile (at “frozen” diffusion) – polymorphic transformation. The transformation into orthorhombic ε-Cu₃Sn and later hexagonal ζ-Cu₁₀Sn₃ are not following the temperature regimes of the bulk equilibrium phase diagram.

Single phase formation of the specific compounds has been seen as future for the interconnect technology. The specific single IMC phase regimes were seen for Cu-Sn nanomultilayers. The scaling criteria have been established to provide control over directed IMC phase formation.

The first nucleated phase at the nano-regime below 100 nm does not depend on the overall composition, what is especially important in context of life cycle analysis of lead free soldering and the approach of minimization of Sn content as the factor of the main environmental impact. It is reasoned in the excess of Gibbs energy associated with internal interfaces. The interfaces can be designed to provide fast diffusion paths for enhancing reaction rates at low temperatures. This discovery supports the targeted development of nano-architectured materials for smart engineering of the joint assembly.
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Part 4 – Final Conclusions and Outlook
Chapter 9. Final Conclusions

In order to formulate rapid bonding method for microelectronic assembly of power modules, the diffusion control needed to be investigated. Through the course of this research, it has been shown that the control thereof affects the solid-state reaction between Cu and Sn, and the formation of the intermediate phases between them. The control over the mass transport was postulated and achieved through two methodological approaches – inhibiting or exploiting the solid-solid reaction.

The inhibition of solid-solid interaction was realised through process conditions – rapid heating rates in conventional Transient Liquid Phase bonding, and through the incorporation of a temporary diffusion barrier coating – Sacrificial Passivation. The exploitation of solid-solid reaction was realised through the architecturing of nano-multilayers and the provision of intimate contact between the thin films of Cu and Sn.

The Cu-Sn system has a limited application for the rapid microelectronic assembly in the conventional Transient Liquid Phase bonding due to its kinetic constraints. The reactive diffusion during heating leads to phase formation of Cu₆Sn₅ and Cu₃Sn and the Cu/Sn interface, before the Sn reaches its melting point. The thicker the compound layer is, the slower the later growth rate of the compound becomes; the later growth is further controlled by the bulk diffusion. The above-mentioned processes define Cu-Sn behaviour during bond formulation. The procedure suffers from a very fundamental rate-limiting step – the kinetics of the interfacial bulk reaction in the solid-state. The rapid heating rates activate the Cu surface by strong overheating. With the heating rates of at least 350 °C/min, the initial interfacial IMC layer is much thinner and allows for quick interfacial transport of the diffusive species. With the sudden overheating the local dissolution and supersaturation of the Cu in liquid Sn is achieved. The bond formation is enhanced by the IMC nucleation and growth within Sn liquid phase. The time required for IMC formation during isothermal solidification is shortened with the enhanced diffusivity.

Sacrificial Passivation, in the form of thin organic film, was applied in order to preclude the early solid-state interdiffusion, but still allowing the subsequent liquid phase reaction to proceed upon heating. The growth rate of the Cu/Sn and
Ag/Sn IMCs follows a parabolic kinetic. The 80 nm PVA as Sacrificial Passivation was effective for the Ag/Sn couple and successfully limited the rate of the interfacial reaction. In contrast, the reaction rates of the Cu/Su couple were not affected by the PVA layer. In order to shorten the diffusion distances, encapsulated powder compact were evaluated. The chemical synthesis methodology enabled formulation of encapsulated metallic particles. The thermally driven deactivation of the Sacrificial Passivation was achieved for Cu and Ag (as reference). The solid-state reaction with Sn powders was quantified. The reaction in Ag-Sn powder mix is tuneable and the highest level of response was observed for powder mix with Ag/SDS. For Cu-Sn powder mix the tailoring of the thermal response is limited, as the solid-state reactive interdiffusion cannot be fully inhibited. Unfortunately, the Sacrificial Passivation approach, although demonstrated successful in slowing down the kinetics of reaction, is not an industrially applicable solution without the chemical study of the solder paste formulation that would also allow the rapid removal of the polymer residues.

Controlled use of reactive diffusion in a solid-state between Cu-Sn was demonstrated on the nano-architectured multilayers. Size effects in the phase formation in Cu-Sn nano-multilayers were observed with the three regimes of the phase formation (nano-regime, transition and bulk like). The nano-regime was established for samples with Cu/Sn thickness below 20 nm. The phase formed at room temperature is the cubic $\delta\text{-Cu}_{11}\text{Sn}_{11}$ regardless of the Cu:Sn ratio, where the initial diffusion leads to the formation and growth of a metastable solution. With raising temperature a more stable phase ($\varepsilon\text{-Cu}_3\text{Sn}$ and later hexagonal $\zeta\text{-Cu}_{10}\text{Sn}_3$) nucleates by the reconstruction of atomic order, without an immediate change of the concentration profile. The transition regime is seen at around the 50 nm thickness of Cu-Sn bi-layer. The hexagonal CuSn phase was observed. The transition occurs as the sample geometry imposes not merely short diffusion distances, but also a large volume of the interfaces that affects the phase formation as the driving factor for the transformations observed. For samples above 100 nm of the bi-layer, the phase formation occurs through (or close to) the bulk reaction path. The phase formation is still very rapid; however the amount of “bulk” atom is enough for the atoms to respond in the way close to the equilibrium.

Specific single IMC phase regimes were observed, which can be particularly interesting for the future of the interconnect technology, as single phase bonds create less obstacles for the electron transport. Most importantly, the scaling criteria
were established to provide control over directed IMC phase formation. The additional Gibbs energy associated with internal interfaces drives the single phase formation upon deposition. The as-deposited interfaces can be designed to provide fast diffusion paths for enhancing reaction rates at low temperatures.

From the experiments carried out during the course of this work, the following conclusions can be made:

(i) Through the theoretical assessment of diffusion kinetics during isothermal solidification, the understanding of the limitations provided by the Cu-Sn systems for the rapid microelectronic assembly was obtained.

(ii) The analysis of heating rate effect on the reaction rate of the liquid-solid bulk interdiffusion in Cu-Sn system was evaluated and chosen as a route to prevent the extensive solid-solid interaction between Cu and Sn during bonding and shorten the time required for the isothermal solidification.

(iii) The heating rate effect was demonstrated experimentally with the design and assembly of the Rapid Thermal Annealing (RTA) furnace.

(iv) The heating rate changes the bond formation mechanism in Cu-Sn. The critical heating rate (350 °C/min) allows for the nuclei growth from the bulk of the liquid Sn to compliment the interfacial IMC growth and shorten the process.

(v) The temporary diffusion barrier coating – Sacrificial Passivation – was applied to preclude the early solid-state interdiffusion, but still allowing the subsequent liquid phase reaction to proceed uninhibited.

(vi) Characterisation of reaction kinetics of passivated diffusion couples was performed to understand the performance of a temporary kinetic barrier indicating a large growth rate reduction (order of magnitude) for passivated Ag-Sn couple. No significant improvement for passivated Cu-Sn was observed.

(vii) Chemical synthesis methodology is suitable for the assembly of the alloy constituents as encapsulated metallic particles. The successful and reliable formulation of the temporary barrier coating and its thermally driven destabilisation was achieved for Cu and Ag particles.
The effect of Sacrificial Passivation on solid-state reaction in sintered powder mix compacts was quantified. The reaction in passivated Ag-Sn powder mix gave an on/off response upon two subsequent heating cycles. The passivation in Cu-Sn powder mix compact was not fully achieved. A solid-state reaction occurred, consuming at least 12 wt.% of present Sn.

Physical vapour deposition is a practical method for the production of the thin films for rapid formation of interconnects. The architecturing of nano-multilayers allows for short diffusion distances, yet provides enough of the volume needed for the proper bonding to occur.

Identification of dominating diffusion species, during reaction diffusion in Cu-Sn thin films, was done with marker experiments. The experiments confirm bulk kinetics in the phase formation behaviour of Cu-Sn indicating the dominant diffusing species in IMC formation being Cu, with a limited diffusion of Sn into Cu over the W marker.

Characterisation of size effects in the initial IMC formation at room temperature of the Cu-Sn nano-multilayers resulted in the determination of critical length scale (< 20 nm Cu/Sn bi-layer) for the demonstration of nano-effects – formation of Cu$_{41}$Sn$_{11}$ instead of Cu$_6$Sn$_5$ was observed regardless of the initial sample composition.

Phase transition upon heating for the nano-regime does not follow the bulk behaviour either. The initial Cu$_{41}$Sn$_{11}$ is transformed into Cu$_3$Sn and upon further heating into Cu$_{10}$Sn$_3$ and Cu$_5$Sn, instead of Cu$_6$Sn$_5$ and Cu in bulk.

Transition region is seen at around 50 nm thickness of Cu-Sn bi-layer. The bulk-alike phase formation is seen the bi-layer above 100 nm in as-deposited state.

These discoveries support the development of smart engineered materials for rapid formation of interconnect, through the application of diffusion control.
Chapter 10. Outlook

In order to formulate the rapid bonding method of Cu and Sn for microelectronic assembly of power modules, the control of the diffusion processes has to be implemented. For the transfer of the results obtained from research into industrial production requires that certain points still to be addressed.

(i) Hindering the solid-state interaction

The rapid heating rate approach is a very useful idea that would be easily transferable into the industrial environment, provided the detailed mechanical characterisation of the joints is performed. Through the use of phase field simulation, the nucleation and IMC growth at rapid heating rates could better understood. Until liquid Sn is still present, the growth of the IMC layers is dominant at low heating rates. The dominant growth of precipitating IMC is observed at high heating rates. The phase field simulations would visualise spatial evolution of the IMC growth over time. For scalability, the masking set-up to achieve proper joint geometry needs to be established and the infrastructure (Rapid Thermal Annealing furnace) must be provided.

The Sacrificial Passivation, although demonstrated successful in slowing down the kinetics of reaction, is not an industrially applicable solution. The absence of the extensive chemical study of the paste formulation would also allow rapid removal of the polymer residues, which were observed during preliminary joining trials.

(ii) Exploiting the solid-state interaction

The investigations of the Cu-Sn nano-multilayer performed show the role of the interfaces in nano-architecture systems. The study of interfaces and their energies requires extensive modelling capabilities. The \textit{ab initio} simulation would provide a profound understanding and quantify the driving forces for the specific phase formation. The atomistic models could be compared against the experimental observations. More generally, knowing that phase formations at the nanoscale do not follow the bulk thermodynamics, the extensive thermodynamic modelling, including interfacial effect should be addressed.
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Appendices
Appendix I

Rapid Thermal Annealing Furnace – design and operation details

Identification of components

The Rapid Thermal Annealing Furnace (RTA) contains of two, independent furnace systems with identical design and function. Each furnace system consists of a chamber, susceptor, thermocouple, temperature controller, thyristor, gas flowmeter and two lamps (Fig. A1.1).

The only common feature to both systems is the lamps water-cooling loop and flowmeter; all four lamps are connected in series by this cooling loop. Furnace temperature is monitored and controlled by the thermocouple placed within the susceptor and wired to the temperature control. The temperature controller receives input from this thermocouple and sends power instructions to thyristor which powers the lamps. Diagrams of the electrical wiring, gas control and water-cooling loop are show in Fig. A1.2.
(b) Electrical

Diagram showing electrical components including fuses, controllers, thyristors, and lamps with connections labeled as 'ground' and '+'.
Fig. A1.2 - Wiring of the RTA, (a) – gas wiring, (b) – electrical wiring, (c) – water wiring.
Capabilities

The RTA is intended for small samples that may lie within the perimeter of the susceptor while not contacting the inner surface of the chamber. Considering the 23.4 mm inner diameter of the chamber and a 20 x 20 x 2 mm susceptor, and the sample clamp, the sample size is limited to less than 10 x 10 x 5 mm.

The RTA is intended for metallic samples. The inclusion of organics in acceptable though should be carefully considered prior to experimentation. Forms of acceptable organics may be binders and flux employed in a soldering process, or other thin coatings. The limitation is to prevent contamination of the chamber.

Reflecting the small size of the samples, the heating and cooling rates are not dependent on the sample mass.

Operation

Cooling water must be turned on prior to furnace operation and maintained at 0.5 l/min according to the flowmeter on the front panel of the furnace. The cooling water loop is run in series through the four lamps of the RTA and its purpose is to maintain a reasonable temperature of the lamp body and has no influence on sample temperature or cooling rate.

Process gas is run in parallel between the two systems; therefore either system can run the gas independently though only a single type of gas can be used for both systems simultaneously. The process gas source should first be verified for type of experiment. The pressure of the gas input into the furnace must be regulated below 10 bars. The flow of gas through the chamber is regulated by the flowmeter on the front panel of the RTA.

Power and Control

Power to the furnace electronics is enabled via the front panel switch. Once on, the temperature controller is the furnace interface and is used to set, program and monitor furnace temperature. The furnace should only be run under a preset temperature profile.
Appendix II

Synthesis guide to encapsulate Ag and Cu particles
Ag particles – Synthesis guide

Chemical Information

- All the chemicals being used
  - Silver Nitrate, AgNO₃ (AgNO₃)
  - Ascorbic acid (AA)
  - Glucose
  - Poly vinyl pyrrolidone (PVP)
  - Polyvinyl Alcohol (PVA)
  - Sodium Dodecyl Sulfate (SDS)
  - Sodium Hydroxide (NaOH)
  - The solvent, Ethylene Glycol (EG)

Silver Nitrate

AgNO₃ (Molecular Weight 169.87 g/mol)
- Appearance: White powder/crystals
- Solubility: H₂O
- Odor: none
- Safety
  - Stability: Stable/Discolours in light
  - Skin: Corrosive; Wash with soap and water immediately
  - Eyes: Corrosive; Flush with plenty of water
  - Inhalation: Extremely destructive to respiratory track; Remove from exposure
  - Carcinogen: none
- Handling: Store in tight container, use gloves and goggles
- Disposal: Dispose of waste and first rinse in salt waste.

http://physchem.ox.ac.uk/MSDS/SI/silver_nitrate.html
http://www.jtbaker.com/msds/englishhtml/s2282.htm
Chemical Information

**Polyvinylpyrrolidone**
(\(\text{C}_6\text{H}_9\text{NO}\)_x, Molecular Weight, monomer, 111.14 g/mol)
- Appearance: White powder
- Solubility: \(\text{H}_2\text{O}\), glycol/polar solvents
- Odor: none
- Safety
  - Stability: Stable
  - Eyes: Irritant; flush with water
  - Inhalation: May cause irritation; remove from exposure
  - Carcinogen: No evidence to cancer in humans
  - Handling: Store in tight container; use goggles and gloves
- Disposal: Waste for organics.

http://www.jtbaker.com/msds/englishhtml/p5290.htm
http://www.pcl.ox.ac.uk/MSDS/PO/polyvinylpyrrolidone.html

Chemical Information

**Polyvinyl Alcohol**
(\(-\text{CH}_2\text{CHOH}\)_x, Molecular Weight, monomer, 44.05 g/mol)
- Appearance: White granules
- Solubility: \(\text{H}_2\text{O}\)
- Odor: mild
- Safety
  - Stability: Stable
  - Eyes: Not expected to be a health hazard
  - Inhalation: Irritant when heated above 200°C; remove from exposure
  - Carcinogen: No evidence to cancer in humans
  - Handling: Store in tight container; use goggles and gloves
- Disposal: Waste for organics.

http://physchem.ox.ac.uk/MSDS/SO/sodium_dodecyl_sulfate.html
http://www.jtbaker.com/msds/englishhtml/s3670.htm

Chemical Information

**Sodium Dodecyl Sulfate**
(\(\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}\) (Molecular Weight 288.38 g/mol)
- Appearance: White fine powder
- Solubility: \(\text{H}_2\text{O}\)
- Odor: 'fatty odor'
- Safety
  - Stability: Stable
  - Eyes: Causes irritation and redness; flush with plenty of water
  - Inhalation: Causes irritation to respiratory tract; remove from exposure
  - Carcinogen: none known
  - Handling: Store in tight container; use gloves and goggles
- Disposal: Waste to organic waste container, including first rinse of beakers and containers.

http://physchem.ox.ac.uk/MSDS/SO/sodium_dodecyl_sulfate.html
http://www.jtbaker.com/msds/englishhtml/s3670.htm

Chemical Information

**Ethylene Glycol**
\(\text{OHC}_2\text{H}_4\text{OH}\) (Molecular Weight 62.07 g/mol)
- Appearance: Colourless, viscous liquid
- Solubility: \(\text{H}_2\text{O}\)
- Odor: "none", semi sweet
- Safety
  - Stability: Stable
  - Eyes: May cause minor irritation; remove contaminated clothing, flush with soap and water
  - Inhalation: Irritation only if heated; remove from exposure
  - Carcinogen: none
  - Handling: Store in tight container; use gloves, goggles, and lab coat
- Disposal: Organic wastes

http://www.jtbaker.com/msds/englishhtml/E5125.htm
http://www.pcl.ox.ac.uk/MSDS/ET/ethylene_glycol.html
Chemical Information

**Ascorbic Acid**
- Formula: C6H8O6 (Molecular Weight 176.13 g/mol)
- Appearance: White powder
- Solubility: H2O
- Odor: none

**Safety**
- Stability: Stable
- Skin: May be irritant; Wash with soap and water
- Eyes: Irritant; Wash
- Inhalation: May cause irritation; remove from exposure
- Carcinogen: none
- Handling: Store in tight container; use gloves and goggles
- Disposal: Dispose of waste and first rinse in Organic Container

http://physchem.ox.ac.uk/MSDS/AS/ascorbic_acid.html
http://www.jtbaker.com/msds/englishhtml/a7608.htm

**Glucose**
- Formula: C6H12O6 (Molecular Weight 180.16 g/mol)
- Appearance: White powder/crystalline powder
- Solubility: H2O
- Odor: none

**Safety**
- Stability: Stable
- Skin: Not expected to be a health hazard
- Eyes: Not expected to be a health hazard; wash thoroughly with water
- Inhalation: Not expected to be a health hazard
- Carcinogen: none
- Handling: Store in tight container; use gloves and goggles
- Disposal: Dispose of waste and first rinse in Organic Container

http://www.jtbaker.com/msds/englishhtml/d0835.htm
http://ptcl.chem.ox.ac.uk/MSDS/GL/alpha-d-glucose.html

**Sodium Hydroxide**
- Formula: NaOH (Molecular Weight 40.00 g/mol)
- Appearance: White powder/crystalline powder
- Solubility: H2O
- Odor: none

**Safety**
- Stability: Stable
- Skin: Corrosive; flush with plenty of water
- Eyes: Corrosive; immediately wash thoroughly with water
- Inhalation: Serve Irritant; Remove immediately from exposure
- Carcinogen: none
- Handling: Store in tight container; use gloves and goggles
- Disposal: Dispose of waste and first rinse in Alkalische container

http://physchem.ox.ac.uk/MSDS/SO/sodium_hydroxide.html
http://www.jtbaker.com/msds/englishhtml/s4040.htm

Reaction Information

**The Reduction Reactions**

The synthesis of silver coated nanoparticles was successfully attempted using three synthesis methods. They differ primarily by reducing agent and reaction temperatures. A brief description of each procedure follows:

**Synthesis Method (A)**: 10 ml of EG was heated to 160 °C for one hour. From separate dropping funnels, solutions of AgNO3 and the organic molecule were added to the system, reacted for one hour, and allowed to cool to room temperature.

**Synthesis Method (B)**: The organic molecule was added to 6 ml of EG and heated to 160 °C for one hour under constant stirring. From separate dropping funnels, solutions of AgNO3 and ascorbic acid were added, reacted for one hour, and allowed to cool to room temperature.

**Synthesis Method (C)**: The organic molecule, glucose, and sodium hydroxide were added to 60 ml of water and brought to 60 °C under constant stirring. A solution of AgNO3 was added react for 10 minutes, and allowed to cool to room temperature.
The Reduction Reactions

Three Oxidation/Reduction reactions occur via three different synthesis. Shown with PVP and the respective reducing agent, similar reactions occur for all caps.

- **Ethylene glycol:**
  
  \[
  2 \text{CH}_2\text{OH} + 2 \text{Ag}^+ + 2 \text{PVP} \rightarrow 2 \text{Ag(PVP)}(s) + 2 e^- + 2 \text{H}^+ \]

- **Ascorbic Acid:**
  
  \[
  \text{Ascorbic Acid} + 2 \text{Ag}^+ + 2 \text{PVP} \rightarrow 2 \text{Ag(PVP)}(s) + 2 e^- \]

- **Glucose:**
  
  \[
  \text{Glucose} + 2 \text{Ag}^+ + 2 \text{PVP} \rightarrow 2 \text{Ag(PVP)}(s) + 2 e^- \]

---

**Reaction Information**

Factors of Reaction

<table>
<thead>
<tr>
<th>Fixed</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor (Ag⁺) concentration [0.25 M]</td>
<td>Synthesis Method</td>
</tr>
<tr>
<td>Reaction Temperature [150 °C or 60 °C]</td>
<td>Polymer</td>
</tr>
<tr>
<td>Ratio of Precursor with Reducing Agent [2:1 with salt]</td>
<td>Addition Rate of Salt</td>
</tr>
<tr>
<td>Nucleation Time [1 hr or 10 min]</td>
<td>Ratio of Precursor with Polymer</td>
</tr>
</tbody>
</table>

Factors were tested at varying ranges

Synthesis Method Vary by Reducing Agent

- Synthesis "A" uses Ethylene Glycol at 180 °C
- Synthesis "B" uses Ascorbic Acid at 160 °C
- Synthesis "C" uses Glucose with a NaOH as a catalyst at 60 °C

Polymer: PVP, PVA, SDS

Molar Ratio of the polymer: 0.5, 1.5, 5.0

Addition Rate: 0.5, 5.0, 50 mL/min

---

**Calculation**

**To Obtain: 0.25 M solution of Ag⁺**

**Route A**

6 mL EG used

\[
0.25 \text{M Ag⁺ solution} = \frac{0.25 \text{M} \times 0.006 \text{L}}{0.006 \text{L}} = 0.25 \text{M Ag⁺ solution} (0.2548 \text{g AgNO₃})
\]

**Route B**

6 mL EG used

\[
0.25 \text{M Ag⁺ solution} = \frac{0.25 \text{M} \times 0.006 \text{L}}{0.006 \text{L}} = 0.25 \text{M Ag⁺ solution} (0.2548 \text{g AgNO₃})
\]

**Route C**

20 mL DI H₂O used

\[
0.25 \text{M Ag⁺ solution} = \frac{0.25 \text{M} \times 0.020 \text{L}}{0.020 \text{L}} = 0.25 \text{M Ag⁺ solution} (0.2548 \text{g AgNO₃})
\]

---

**Calculation**

**To Obtain: Ratios of Reduction Agent and Capping Agent**

**Route A**

Reducing agent is the solvent and the ratio is based on its volume. It works out to be about 70:1

**Route B**

**Route C**

Polymer

Molar Ratio of the polymer: 0.5, 1.5, 5.0

Addition Rate: 0.5, 5.0, 50 mL/min
Reaction

**Necessary Glassware**

1. Used for Massing Chemicals
   - 2 small beakers
   - 2 spatulas*
   - 1 weighing boat (not shown)
2. Used in Reaction
   - round bottom flask
   - 2 graduated cylinders
   - 2 addition droppers
3. Used for Collection
   - 12 centrifuge tubes**
   - 2 sample vials

*Used throughout synthesis
**Synthesis Method C needs 24 centrifuge tubes

---

**Reaction**

**Synthesis Route A**

1. Massing the Chemicals
   - Record all masses and observations in a lab notebook.
   - Obtain needed chemicals
   - AgNO₃, 0.2548 g
   - EG, 18 mL
   - THE CAP: PVP, PVA, or SDS.
   - Mass is a variable
   - (see Taguchi Array and calculations)
   - Place a paper towel on the desk
   - Weigh all chemicals
   - Use beakers for the salt and reducer and a weighing boat for the cap.

---

2. Reaction
   - Add the 6 mL EG to the flask with a stir bar.
   - Turn on the heat and stirring on the mantle. The temperature on the mantle does not change.
   - Set the thermostat to well over 200°C. This yields a reaction temperature of 160°C.
   - Close the system (glass cap) and insert the thermometer to verify system’s temperature. Be sure the thermometer does not interfere with the stirring.
   - It will take at least 1 hr to reach 160°C

---

3. Addition
   - The solutions will take some time to dissolve.
   - Begin mixing the polymer before you leave the lab!
   - Add 6 mL EG to the beaker of the capping agent and place it on the stirring mantel with low heat.
   - SOLUTIONS MUST BE DISSOLVED!!

---

**Synthesis Route A**

**Reaction**

3. Addition
   - The solutions will take some time to dissolve.
   - Begin mixing the polymer before you leave the lab!
   - Add 6 mL EG to the beaker of the capping agent and place it on the stirring mantel with low heat.
   - SOLUTIONS MUST BE DISSOLVED!!
Addition

Transfer solutions to addition funnels.

Make sure it's closed!!

Set up droppers on flask.

Addition rate of the salt

Three Addition rates were previously used:

Rate 1 = 50 mL/min = “fast”

= completely open

Rate 2 = 5 mL/min = “moderate”

= slow continuous drop

Rate 3 = 0.5 mL/min = “very slow”

= 1 drop every 15 sec

Add salt and cap to the system.

Observe colour changes to the system

Let the system react for 1 hr while stirring at 160 °C.

Turn off the heat and stirrer and let the system cool.

This will take about 45 mins.

Note the colour of the system. It should be the colour of liquid clay: light tan/grey and a bit cloudy.

Dilute the system with about 25x the volume with DI water (about 500 mL).

Use a spatula to scrape the solid from the inside of the flask. Collect as much as possible from the reaction vessel.

Fill 12 0-tubes to about 45 mL each

Place tubes in the green holders and be sure the weight is balanced inside.

Set to 4000 rpm for 30 min

After 30 mins get the tubes, bring them to the lab, and discard the supernatant in the organic waste jar.

The centrifugation is repeated 4 times. Acetone is used for remaining centrifugations. As the supernatant gets more clear in colour, the volume of acetone may be lessened. If at the end it’s not clear, repeat centrifugation.

After second centrifugation, scrape the walls of the tubes to re-disperse particles.

Describe the consistency or colour of the particles.
5. Collection
- Collect only after supernatant returns clear from centrifuge. Discard as much as possible without losing solids.
- Add a little ethanol and use the spatula to scrape the particles from the sides into the centre.
- Get 2 sample vials
  - One vial is for the wet sample (along with the contents from two c-tube)
  - One vial is for the dry sample (along with the contents from the other four c-tubes)
- Label them

6. Drying
- Store particle in the decicator in the hood until needed.
- XRD, TGA, and DSC require dry particles. It is best to only vacuum dry them slightly before analysis (i.e., the night before)

1. Massing the Chemicals
- Record all masses and observations in a lab notebook.
- Obtain needed chemicals
  - AgNO₃ 0.2548 g
  - Ascorbic Acid 0.528 g
  - THE CAP: PVP, PVA, or SDS. Mass is variable
  - EG 12 mL
  - 6 mL DI H₂O
- Place a paper towel on the table
- Weigh everything at the beginning
- Use beakers for the salt and reducer and a weighing boat for the cap.

2. Reaction
- Add the capping agent to the flask first with 6 mL EG. Add a stir bar.
- Turn on the heat and stirring on the mantle. The temperature on the mantle does not change.
- Set the thermostat to well over 200°C. This yields a reaction temperature of 160°C.
- Close the system and insert the thermometer to verify system's temperature. Be sure the thermometer does not interfere with the stirring.
- It will take about 1 hr to reach 160°C
3. Addition

Prepare solutions after the system has reached 160 °C

Add 6 mL water to the beaker of Ascorbic Acid. Dissolve with manual stirring.

Add 6 mL EG to the beaker of Ag+. Mix it on the stirring mantle for 10 mins on low heat and moderate stirring.

SOLUTIONS MUST BE DISSOLVED!!

Add salt and cap to the system.

Observe colour changes to the system.

30

“Transfer solutions to addition funnels.
• Make sure its closed!!
• Set up droppers on flask.
• Addition rate of the salt

Three Addition rates were previously used
• Rate 1 = 50 mL/min = “fast”
  = completely open
• Rate 2 = 5 mL/min = “moderate”
  = slow continuous drop
• Rate 3 = 0.5 mL/min = “very slow”
  = 1 drop every 10 sec

Add salt and cap to the system.

Observe colour changes to the system.

4. Centrifuge

Dilute the system with about 25x the volume with DI water (about 500 mL)
• Use a spatula to scrape the solid from the inside of the flask. Collect as much as possible from the reaction vessel.
• Fill 12 c-tubes to about 45 mL each
• Place tubes in the green holders and be sure the weight is balanced inside.
• Set to 4000 rpm for 30 min.

Let the system react for 1 hr while stirring at 160 °C.
• Turn off the heat and stirrer and let the system cool. This will take about 45 mins.
• Note the colour of the system.
After 30 mins get the tubes, bring them to the lab, and discard the supernatant in the organic waste jar.

The centrifugation is repeated 4 times. Acetone is used for remaining centrifugations. As the supernatant gets more clear in colour, the volume of acetone may be lessened. If at the end it's not clear, repeat centrifugation.

After second centrifugation, scrape the walls of the tubes to re-disperse particles.

Describe the consistency or colour of the particles.

---

**Collection**

Collect only after supernatant returns clear from centrifuge. Discard as much as possible without losing solids.

Add a little ethanol and use the spatula to scrape the particles from the sides into the centre.

Get 2 sample vials

- One vial is for the wet sample (along with the contents from two c-tube)
- One vial is for the dry sample (along with the contents from the other four c-tubes)

Label them

---

**Drying**

Store particle in the decicator in the hood until needed. XRD, TGA, and DSC require dry particles. It is best to only vacuum dry them shortly before analysis (i.e., the night before)

---

**Massing the Chemicals**

Record all masses and observations in a lab notebook.

Obtain needed chemicals

- Ag⁺ 0.8548 g
- Glucose 1.80 g
- NaOH 0.30 g
- THE CAP: PVP, PVA, or SDS, Mass is a variable, (see Taguchi Array and calculations)
- 80 mL DI water

Place a paper towel on the table
Weigh everything at the beginning.
Use beakers for the salt and reducer and a weighing boat for the cap.
2. Reaction

"Add the capping agent, glucose, NaOH and 60 mL water to the flask with a stir bar. Turn on the heat and stirring on the mantle. Set the thermostat to 110 °C. This yields a reaction temperature of 60 °C. Close the system (glass cap) and insert the thermometer to verify system’s temperature. Be sure the thermometer does not interfere with the stirring. It will take about 30 min to reach 60 °C"

3. Addition

"After the system has reached 60 °C, add 20 mL of water to the beaker of AgNO3, Dissolve. Add Ag+ solution to addition funnels. Make sure its closed!! Set up droppers on flask. Three Addition rates were previously used Rate 1 = 50 ml/min = “fast” completely open Rate 2 = 5 mL/min = “moderate” slow continuous drop Rate 3 = 0.5 mL/min = “very slow” 1 drop every 10 sec Add salt to the system. Observe colour changes to the system. All the reaction to proceed for 10 min and remove it from heat, allowing it to cool."

4. Centrifuge

"Dilute the system with about 15x the volume with DI water (about 1000 mL) Use a spatula to scrape the solid from the inside of the flask. It is important to collect as much as possible Use a large beaker to collect everything. Fill 24 c-tubes to about 50 mL each Place tubes in the green holders and be sure the weight is balanced inside. Set to 4000 rpm for 30 min"

"After 30 mins get the tubes, bring them to the lab, and discard the supernatant in the organic waste jar. The centrifugation is repeated 4 times. Acetone is used for remaining centrifugation. As the supernatant gets more clear in colour, the volume of acetone may be lessened. If at the end its not clear, repeat centrifugation. If able to, after second centrifugation, scrape the walls of the tubes to redisperse particles. Describe the consistency or colour of the particles."
5. Collection
- Collect only after supernatant returns clear from centrifuge. Discard as much as possible without losing solids.
- Add ethanol and use the spatula to scrape the particles from the sides into the center.*** If 'blob-like'. See slide 47
- Get 2 sample vials
  - One vial is for the wet sample (along with the contents from two c-tube)
  - One vial is for the dry sample (along with the contents from the other four c-tubes)
- Label them

6. Drying
- Store particle in the decicator in the hood until needed.
- XRD, TGA, and DSC require dry particles. It is best to only vacuum dry them shortly before analysis (i.e., the night before)

Appendix

How to Correctly Mass a Sample
- Using a dry beaker on the scale, zero out the balance by pressing "tare"
- Remove chemical and place amount inside
- Place back on balance until you have reached your mass
- If there are solids in the scale, use ethanol to clean.

How to work the thermostat
1. Spin top to change temperature
2. Mark is about 50 degrees different from actual temperature. This difference increases as temperature increases.
Appendix

How to Set the Oven

1. Insert sample, close door, and change handle to “VAC. ON”
2. Hit “mode” button for temperature and arrows to change temperature to 50 C
3. Turn on the pump.
4. Close Air and Gas knobs. If the gauge doesn’t move down, then check the handle to the oven’s door and sort of push in (sometimes the lock doesn’t quite lock.)

Appendix

How to Cleaning Centrifuge Tubes

1. It should be done readily after using or the solids become difficult to remove.
2. Use soap (Alconox) and water first. This is a really good soap for all glassware. You need little of it.
3. If there is still solids present, then use 5:1 solution of water and HNO₃ (Nitric Acid)
   Always add acid to water!
4. After adding the Acid/Water solution to the c-tube, wait about 2 mins and then dilute heavily with water. This should rid any remaining solids from the tube.
5. Rinse caps, too.
6. Place tubes in the rack to dry.

Appendix

Observations for Ag np synthesis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before Addition</th>
<th>With Acid and dil.</th>
<th>With Sodium/acetone add.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1</td>
<td>Clear</td>
<td>Light yellow</td>
<td>Light brown</td>
</tr>
<tr>
<td>1,2</td>
<td>Yellow/Green</td>
<td>Light mustard</td>
<td>Tan</td>
</tr>
<tr>
<td>1,3</td>
<td>Clear</td>
<td>Light brown</td>
<td>Tan</td>
</tr>
<tr>
<td>2,1</td>
<td>Light brown</td>
<td>Light brown</td>
<td>Tan</td>
</tr>
<tr>
<td>2,2</td>
<td>Gray/White</td>
<td>Medium brown, solid</td>
<td>Tan</td>
</tr>
<tr>
<td>2,3</td>
<td>Black powder</td>
<td>Dark tan</td>
<td>Tan</td>
</tr>
<tr>
<td>3,1</td>
<td>Yellow/Green</td>
<td>Brown, “no solids”</td>
<td>Tan</td>
</tr>
<tr>
<td>3,2</td>
<td>Medium brown</td>
<td>Tan</td>
<td>Tan</td>
</tr>
<tr>
<td>4,1</td>
<td>Clear</td>
<td>Grey/brown</td>
<td>Tan</td>
</tr>
<tr>
<td>4,2</td>
<td>Yellow/Green</td>
<td>White</td>
<td>Tan</td>
</tr>
<tr>
<td>4,3</td>
<td>Yellow/Green</td>
<td>Brown, solids</td>
<td>Tan</td>
</tr>
<tr>
<td>5,1</td>
<td>Grey/green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>5,2</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>6,1</td>
<td>Clear/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>6,2</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>6,3</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>6,4</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>7,1</td>
<td>Grey/green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>7,2</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>7,3</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>7,4</td>
<td>Green/brown</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>8,1</td>
<td>Clear/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>8,2</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>8,3</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>8,4</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>9,1</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>9,2</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>9,3</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>9,4</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
<tr>
<td>9,5</td>
<td>Yellow/Green</td>
<td>Black</td>
<td>Tan</td>
</tr>
</tbody>
</table>

Problems with Ag np synthesis

1. Appearance: Often while performing the synthesis, the colour of the solution or particles will not always match my notes. Continue with synthesis from start to finish. Perhaps it is worth to use XRD to verify the phase of the solid. Even if it means repeating the synthesis, it is better to know that the product is still correct for later!
2. Collection: The samples from trials 7-9 show that if we use Synthesis Method C, the samples from trials 7-9 show that if we use Synthesis Method C, the particles are often ‘blob like’ rather than particle like. This being the case, they will really never become particle like while centrifuging. Before collection, use extra acetone with extra centrifugation cycles. This will help. Use drop pens and spatulas to collect as much as possible in ethanol. They will look more dry after using the oven.
Appendix
Quick Reference

Synthesis Method A

- Mass chemicals (Ag+ (0.2548g), Cap, EG (18mL))
- Heat 6 mL EG under stirring; \( T=160 \, ^\circ \text{C} \)
- Add salt and cap in EG at addition rate; t_{rxn}=1 \, hr
- Remove from heat
- Add 500 mL DI Water \& centrifuge
- Repeat centrifuge until supernatant is clear
- Collect in eth-ol.

Synthesis Method C

- Mass chemicals (Ag+ (0.2548), Cap, AA (0.528), EG(12 mL), water (6mL))
- Heat 6 mL EG and cap under stirring; \( T=160 \, ^\circ \text{C} \)
- Add salt and AA at addition rate; t_{rxn}=1 \, hr
- Remove from heat
- Add 500 mL DI Water \& centrifuge
- Repeat centrifuge until supernatant is clear
- Collect in eth-ol.

Synthesis Method C

- Mass chemicals (Ag+ (0.8548), Cap, Glucose (1.80g), NaOH (0.30 g), water (80 mL))
- Heat 60 mL water, cap Glucose, NaOH under stirring; \( T=60 \, ^\circ \text{C} \)
- Add salt in water at addition rate; t_{rxn}=10 \, min
- Remove from heat
- Add 1000 mL DI Water \& centrifuge
- Repeat centrifuge until supernatant is clear
- Collect in eth-ol.
Cu particles – Synthesis guide

Chemical Information

- All the chemicals being used
  - Copper sulfate pentahydrate, CuSO4•5H2O (Cu+++)
  - Ascorbic acid (As)
  - Poly vinyl pyrrolidone (PVP)
  - Sodium Dodecyl Sulfate (SDS)
  - The solvent, Ethylene Glycol (EG)

Copper Sulfate Pentahydrate

- Appearance: Blue solid crystals
- Solubility: H2O and glycol
- Odor: none
- Safety
  - Stability: Stable
  - Skin: May be irritant, non-toxic; if exposed, wash with soap and water
  - Eyes: Irritant; flush with water
  - Inhalation: May cause irritation; remove from exposure
  - Carcinogen: none
  - Handling: Store in tight container; use goggles and gloves
  - Disposal: Waste for salts (including first rinse with H2O of beakers and containers)

Chemical Information

- http://physchem.ox.ac.uk/MSDS/CO/copper_II_sulfate.html
Chemical Information

Ascorbic Acid

\( \text{C}_6\text{H}_8\text{O}_6 \) (Molecular Weight 176.13 g/mol)

- Appearance: White powder
- Solubility: \( \text{H}_2\text{O} \)
- Odor: none
- Safety:
  - Stability: Stable; \( \text{H}_2\text{O} \) Solutions may oxidize in air
  - Skin: May be irritating; wash with soap and water
  - Eyes: Irritant; wash
  - Inhalation: May cause irritation; remove from exposure
  - Carcinogen: none
- Handling: Store in tight container; use gloves and goggles
- Disposal: Dispose of waste and first rinse in Organic Container

http://physchem.ox.ac.uk/MSDS/AS/ascorbic_acid.html
http://www.jtbaker.com/msds/englishhtml/a7608.htm

Chemical Information

Polyvinylpyrrolidone

\((\text{C}_6\text{H}_9\text{NO})_x\) (Molecular Weight, monomer, 111.14 g/mol)

- Appearance: White powder
- Solubility: \( \text{H}_2\text{O} \), glycol/polar solvents
- Odor: none
- Safety:
  - Stability: Stable
  - Skin: May be irritating, non-toxic; wash with soap and water
  - Eyes: Irritant; flush with water
  - Inhalation: May cause irritation; remove from exposure
  - Carcinogen: No evidence to cancer in humans
- Handling: Store in tight container; use goggles and gloves
- Disposal: Waste for organics.

http://www.jtbaker.com/msds/englishhtml/p5290.htm
http://www.pcl.ox.ac.uk/MSDS/PO/polyvinylpyrrolidone.html

Chemical Information

Sodium Dodecyl Sulfate

\( \text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na} \) (Molecular Weight 288.38 g/mol)

- Appearance: White fine powderflake-like
- Solubility: \( \text{H}_2\text{O} \)
- Odor: fatty odor
- Safety:
  - Stability: Stable
  - Skin: Mild irritant; flush immediately with soap and water
  - Eyes: Causes irritation and redness; flush with plenty of water
  - Inhalation: Causes irritation; remove from exposure
  - Carcinogen: none known
- Handling: Store in tight container; use gloves and goggles
- Disposal: wastes to organic waste container, including first rinse of beakers and containers.

http://physchem.ox.ac.uk/MSDS/SO/sodium_dodecyl_sulfate.html
http://www.jtbaker.com/msds/englishhtml/s3670.htm

Chemical Information

Ethylene Glycol

\( \text{OHC}_2\text{H}_4\text{OH} \) (Molecular Weight 62.07 g/mol)

- Appearance: Colourless viscous liquid
- Solubility: \( \text{H}_2\text{O} \)
- Odor: ‘none’, Semi sweet
- Safety:
  - Stability: Stable
  - Skin: May cause minor irritation; remove contaminated clothing, flush with soap and water
  - Eyes: Splashes may cause irritation; flush with water
  - Inhalation: Irritation only if heated, remove from exposure
  - Carcinogen: none
- Handling: Store in tight container; use gloves, goggles, and lab coat
- Disposal: Organic wastes

http://www.pcl.ox.ac.uk/MSDS/ET/ethylene_glycol.html
http://www.jtbaker.com/msds/englishhtml/E5125.htm
The Reduction Reaction

Ascorbic Acid

Reducing Agent

\[ \text{Cu}^{2+} + \text{Ascorbic Acid} \rightarrow \text{Cu} \text{(Ascorbic acid) } \]

Salt with Sodium Dodecyl Sulfate

(Capping Agent)

Salt with Polyvinylpyrrolidone

(Capping Agent)

\[ \text{Cu}^{2+} + \text{Salt with PVP} \rightarrow \text{Cu} \text{(PVP) } \]

\[ \text{Cu}^{2+} + \text{Salt with SDS} \rightarrow \text{Cu} \text{(SDS) } \]

The Net Reaction

\[ \text{Ascorbic Acid} + \text{Cu}^{2+} \rightarrow \text{Cu} \text{(Ascorbic acid) } \]

Factors of Reaction

Fixed
- Precursor (Cu+2) amount [0.0015 mol]
- Ratio of Precursor with Reducing Agent [2:1]
- Reaction Temperature [140 °C]
- Nucleation Time [2 hr]

Variable
- Polymer
- Addition Rate of Salt
- Ratio of Precursor with Polymer

Factors were tested at varying ranges
- Polymer: PVP & SDS
- Addition Rate: 5 ml/min & 50 ml/min
- Molar Ratio of the polymer: 0.5 & 1.5

Calculations

To Obtain: 0.0015 mol Cu+2

\[ 0.0015 \text{ mol Cu}^{2+} = \left( \frac{1 \text{ mol CuSO}_4 \cdot 5 \text{H}_2\text{O}}{1 \text{ mol Cu}^{2+}} \right) \left( \frac{249.68 \text{ g CuSO}_4 \cdot 5 \text{H}_2\text{O}}{1 \text{ mol CuSO}_4 \cdot 5 \text{H}_2\text{O}} \right) = 0.3748 \text{ g CuSO}_4 \cdot 5 \text{H}_2\text{O} \]

2:1 Ratio of Cu+2: Ascorbic Acid

\[ 0.0015 \text{ mol CuSO}_4 \cdot 5 \text{H}_2\text{O} \left( \frac{1 \text{ mol CuSO}_4 \cdot 5 \text{H}_2\text{O}}{1 \text{ mol Ascorbic Acid}} \right) \left( \frac{176.13 \text{ g Ascorbic Acid}}{1 \text{ mol Ascorbic Acid}} \right) = 0.5286 \text{ g Ascorbic Acid} \]

x:1 Ratio of Cu+2: Polymer

\[ 0.0015 \text{ mol CuSO}_4 \cdot 5 \text{H}_2\text{O} \left( \frac{1 \text{ mol polymer}}{1 \text{ mol CuSO}_4 \cdot 5 \text{H}_2\text{O}} \right) \cdot \frac{x}{2} = \frac{x}{2} \text{ g polymer} \]

\[ x = \frac{M_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}{M_{\text{polymer}}} \]

\[ x = 0.5 \]

Use of factors at 10 levels of the factors (i.e., 10 levels of polymer)

\[ x_1 = 11 \text{ Hg mol PVP} \quad x_2 = 238.43 \text{ Hg mol SDS} \]

Mass of polymer used in acid:

\[ x_1 = 0.0035 \text{ g PVP} \quad x_2 = 0.0196 \text{ g SDS} \]

\[ x_1 = 0.24 \text{ mg SDS} \quad x_2 = 0.41 \text{ mg SDS} \]

Necessary Glassware

1. Used for Massing Chemicals
   - 2 small beakers
   - 2 spatulas*
   - 1 weighing boat (not shown)

2. Used in Reaction
   - Round bottom flask
   - 2 graduated cylinders
   - 2 addition droppers

3. Used for Collection
   - 6 centrifuge tubes
   - 2 sample vials

*Used throughout synthesis
1. Chemicals
- Record all masses and observations in a lab notebook.
- Obtain needed chemicals
- SALT: Cu²⁺ 0.3735 gr
- REDUCER: aa 0.528 gr
- CAP: PVP or SDS.
- Mass is a variable (see Taguchi Array & calculations)
- 20 mL EG
- 10 mL DI H₂O
- Place a paper towel on the desk
- Weigh all chemicals
- Use beakers for the salt and reducer and a weighing boat for the cap.

2. Reaction
- Add the capping agent to the flask with 10 mL EG with a stir bar,
- Turn on the heat and stirring on the mantle. The temperature on the mantle does not change.
- Set the thermostat to over 200 C. This yields a reaction temperature of 140 C.
- Close the system (glass cap) and insert the thermometer to verify system's temperature.
- Be sure the thermometer does not interfere with the stirring.
- It will take about 1 hr to reach 140 C

3. Addition
- After system has reached 140 °C, prepare Addition solutions.
- Mix Cu²⁺ stirring mantel on low heat with moderate stirring until dissolved.
- SOLUTIONS MUST BE DISSOLVED!!
- Transfer solutions to addition funnels.
- Make sure its closed!!
- Addition Rate of salt
  - Two rates were used
  - Rate 1 = 5 ml/min = "slow"
  - Rate 2 = 50 ml/min = "fast"
- Set up droppers onto flask and add at rate
- Observe colour changes to the system.
Let the system react for 1 hr, stirring at 140°C.

Add a “pinch” of ascorbic acid and change the temperature to 80°C (marked 120 on the thermostat).

The reaction will proceed for 1 hr.

After this time, turn off the heat and stirrer and let the system cool. This will take about 45 mins.

Note the colour of the system. It should be a reddish-brown hue.

### 4. Centrifuge

- Use 300 mL of Ethanol for centrifugation. Add it to the flask and use a spatula to scrape the solid from the inside of the flask. Collected as much as possible.
- Fill 6 centrifuge tubes to 50 mL.
- Place tubes in the green holders and be sure the weight is balanced inside.
- Set to 4000 rpm for 30 mins.

### 5. Collection

- Collect only after supernatant returns clear from centrifuge. Discard.
- Use the spatula to scrape the particles from the sides into the centre. There will be residual ethanol from centrifuge. This is helpful to transfer particles.
- Get 2 sample vials and pipette 1 “full pipette” (about 2 mL) of ethanol into each.
  - One vial is for the wet sample (along with the contents from two c-tube).
  - One vial is for the dry sample (along with the contents from the other four c-tubes).
- Label them.
Reaction
6. Drying
   - XRD, TGA, and DSC require dry particles.
     Only vacuum dry them shortly before analysis (i.e., the night before)

Appendix
How to Correctly Mass a Sample
- Using a dry beaker on the scale, zero out the balance by pressing "tare"
- Remove chemical and place amount inside
- Place back on balance until you have reached your mass
- If there are solids in the scale, use ethanol to clean.

Appendix
How to work the thermostat
1. Spin top to change temperature
2. Mark is about 50 degrees different from actual temperature. This difference increases as temperature increases.

Appendix
How to Set the Oven
1. Insert sample, close door, and change handle to "VAC. ON"
2. Hit "mode" button for temperature and arrows to change temperature to 50 C
3. Turn on the pump.
4. Close Air and Gas knobs. If the gauge doesn't move down, then check the handle to the oven's door and sort of push in (sometimes the lock doesn't quite lock.)
Appendix

How to Cleaning Centrifuge Tubes

1. It should be done readily after using or the solids become difficult to remove.
2. Use soap (Alconox) and water first. This is a really good soap for all glassware. You need little of it.
3. If there is still solids present, then use 5:1 solution of water and HNO₃ (Nitric Acid). Always add acid to water!
4. After adding the Acid/Water solution to the c-tube, wait about 2 mins and then dilute heavily with water. This should rid any remaining solids from the tube.
5. Rinse caps, too.
6. Place tubes in the rack to dry.

Appendix

Observations for Cu np synthesis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colour at Addition</th>
<th>Colour at Cooling</th>
<th>Colour of 1st Supernatent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_3</td>
<td>light pink</td>
<td>red</td>
<td>orange</td>
</tr>
<tr>
<td>2_3</td>
<td>medium pink</td>
<td>burnt orange</td>
<td>orange</td>
</tr>
<tr>
<td>3_2</td>
<td>pink</td>
<td>red</td>
<td>dark red</td>
</tr>
<tr>
<td>4_3</td>
<td>light pink</td>
<td>dark orange</td>
<td>orange</td>
</tr>
<tr>
<td>5_4</td>
<td>pink</td>
<td>dark red</td>
<td>orange</td>
</tr>
<tr>
<td>6_2</td>
<td>light pink</td>
<td>brown</td>
<td>brown</td>
</tr>
<tr>
<td>7_2</td>
<td>light pink</td>
<td>orange</td>
<td>red-brown</td>
</tr>
<tr>
<td>8_2</td>
<td>pink</td>
<td>brown</td>
<td>brown</td>
</tr>
</tbody>
</table>

Appendix

Quick Reference

- Mass Chemicals
  - Cu²⁺ 0.3745 gr
  - AA 0.528 g
  - PVP (0.0838 or 0.2506 g)
  - SDS (0.2163 or 0.7210 g)
  - 20 mL Eg
  - 10 mL DI H₂O
- Heat polymer and 10 mL EG under stirring; ΔT=140 °C
- Add salt and AA at addition rate; Δtₐₐ=1 hr
- Add a pinch of AA and ΔT=80 °C; Δtₐₑ=1 hr
- Remove from heat
- Vₜ=300 mL eth-ol → centrifuge
- Repeat centrifuge until supernatant is clear
- Collect in eth-ol.
Appendix III

Formation enthalpies for Cu-Sn IMC phases

Change of formation enthalpy of Cu-Sn IMC for different compositions and at different temperatures as obtained from Thermo-Calc.

Fig. A3.1 – Enthalpy of formation for Cu-Sn compounds at 30 °C.
Fig. A3.2 – Enthalpy of formation for Cu-Sn compounds at 130 °C.

Fig. A3.3 – Enthalpy of formation for Cu-Sn compounds at 200 °C.
Fig. A3.4 – Enthalpy of formation for Cu-Sn compounds at 260 °C.

Fig. A3.5 – Enthalpy of formation for Cu-Sn compounds at 300 °C.
Fig. A3.6 – Enthalpy of formation for Cu·Sn compounds at 360 °C.

Fig. A3.7 – Enthalpy of formation for Cu·Sn compounds at 450 °C.
Fig. A3.8 – Enthalpy of formation for Cu-Sn compounds at 630 °C.

Fig. A3.9 – Enthalpy of formation for Cu-Sn compounds at 760 °C.
Appendix IV

Interaction of W diffusion barrier in Cu-Sn nano-multilayers

As shown in the Chapter 8, it is possible to produce a nano-multilayer Cu-Sn filler metal foil that undergoes rapid phase transformation into thermally stable intermetallic compound(s). It is possible due to the instant interdiffusion. The control of the reaction rate was intended by changing the interlayer thickens. The temperature regimes of the transformations were confirmed, however the control of the timing was not yet assured. With this purpose, an ultra-thin diffusion barrier coating of W was introduced after each of Cu and Sn layer, separating the intimate contact between the layers. The literature states W wires and films being successfully applied as inert markers. Additionally, thick W film is industrially used as the diffusion barrier against Cu. The W was chosen upon the lack of the formation of solid solution with Cu, and Sn (based on the fact Sn-W is one of the binary systems with an unknown phase diagram). Also such ultra-thin film was previously used (Chapter 8) as the marker to analyse diffusion kinetics in thin film geometry of Cu/Sn diffusion couple and shown no interaction with the either Cu or Sn, yet allowed for the interdiffusion of the atoms through it. The idea was to separate the highly interacting Cu and Sn nano-layers and temporary stabilize the nano-multilayer filler and obtain a control mechanism over the Cu-Sn interdiffusion (Tab. A4.1 Fig. A4.1).

![Fig. A4.1 – Sketch of the Cu/W/Sn/W multilayer geometry.](image)

The nano-multilayered samples of Cu/W/Sn/W were deposited on the Si substrate with the SiOx/SiNx barrier coating by means of physical vapour deposition without breaking vacuum and analysed using GI-XRD, RBS (only for the thinnest sample) and electron microscopy. The list of Cu/Sn nano-multilayers with W diffusion barrier coating investigated is given in Tab. A4.1.
Tab. A4.1. As-designed geometry of Cu-Sn nanomultilayers with incorporated W barrier coating with 3:2 Cu/Sn ratio and three Cu-Sn bi-layer thickness regimes.

<table>
<thead>
<tr>
<th>Cu:Sn ratio</th>
<th>thickness of the bi-layer (aCu/W/bSn/W) x10, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:2</td>
<td>(9Cu/W/6Sn/W) (30Cu/W/20Sn/W) (90Cu/W/60Sn/W)</td>
</tr>
</tbody>
</table>

Description of 9 nm Cu/W 6 nm Sn/W samples

A typical topography of as-deposited sample is given in Fig. A4.2. It shows uniform fine grained structure. Upon in-situ XRD (after exposure up to 450 °C) the structure seems to be denser, but with a visible fraction of intergranular voids (Fig. A4.3).

![Fig. A4.2 – Topography of as-deposited of 3:2 ratio nano-multilayers (9Cu/W/6Sn/W)x10: (a) SEM plain view; SE, 20 kV. (b) AFM tapping (5 μm x 5 μm) and (1 μm x 1 μm).](image)

![Fig. A4.3 – Topography of upon the in-situ HT-XRD thermal exposure at maximum of 450 °C of 3:2 ratio nano-multilayers (9Cu/W/6Sn/W)x10: SE, 20 kV.](image)

The cross-section of as-deposited state is seen in Fig. A4.4. The sample shows a clearly visible multi-layered nature. Initial Cu layer at the substrate is very flat. The subsequent layers have a wavy character, which enhances with the distance from the substrate. The interdiffusion between the layers in as-deposited state cannot be fully excluded, however EDX analysis indicates the clear multilayer composition.
The RBS analysis (Fig. A4.5) confirms the separation of the metallic layers. Though, the interdiffusion or sample roughness affects the sharpness of Cu peaks.

In-situ heating with XRD in grazing incident setup was used to identify the phase composition. The experimental results for 9Cu/W/6Sn/W during in-situ heating up to 300 °C are presented in Fig. A4.6. Upon the analysis it was not possible to form a conclusion on the phase identification. The position of main Cu 111, Sn 200 and W 111 peaks is marked in the chart. The region between 40°-43.5° 2theta is marked as the Cu·Sn IMC region. The peaks of different IMC phases – Cu₆Sn₅, Cu₁₀Sn₃ and Cu₄₁Sn₁₁ are present in that 2theta region.
Fig. A4.6 – Set of chosen normalised diffractograms at 30·300 °C for (9Cu/W/6Sn/W)x10: GI-XRD, theta-2theta (20·80°).

The peaks are broad over the temperature range. Possibly due to the small grain sizes or high stresses in the system. The shape of the main peak evolves with the temperature. The initially two separate peaks merge upon reaching 300 °C.
Description of 30 nm Cu/W 20 nm Sn/W samples

A typical topography of as-deposited sample is given in Fig. A4.7. It shows uniform, fine grained structure.

![Fig. A4.7 – Topography of as-deposited of 3:2 ratio nano-multilayers (30Cu/W/20Sn/W)x10: (a) SEM plain view; SE, 20 kV; (b) AFM tapping (5 µm x 5 µm) and (1 µm x 1 µm).](image1)

The cross-section of as-deposited state is seen in Fig. A4.8. The sample has a clearly visible multi-layered structure. The layers are wavy and voids in the structure are seen.

![Fig. A4.8 – STEM cross-section view of as-deposited nano-multilayers (30Cu/W/20Sn/W)x10.](image2)

Phase identification was performed upon in-situ heating with XRD in grazing incident setup. The experimental results for 30Cu/W/20Sn/W during in-situ heating up to 300 °C are presented in Fig. A4.9. Upon the analysis it was not possible to clearly identify the phases present in the sample. The position of main Cu 111, Sn 200 and W 111 peaks is marked in the chart. The region between 40°-43.5° 2theta is marked as the Cu-Sn IMC region. The peaks of different IMC phases – Cu₆Sn₅, Cu₁₀Sn₃ and Cu₄₁Sn₁₁ are present in that 2theta region.
Fig. A4.9 – Set of chosen normalised diffractograms at 30-300 °C for 
(30Cu/W/20Sn/W)x10: GI-XRD, theta-2theta (20-80°).

From room temperature up to 200 °C the main peak reflects the Cu 111 position. At 300 °C it shifts into the position matching Cu_{10}Sn_{3} 300 reflex.
Description of 90 nm Cu/W 60 nm Sn/W samples

A typical topography of the samples in as-deposited and after in-situ heating exposure up to 450 °C is given in Fig. A4.10. The polycrystalline columnar structure of the film is seen for the both cases (in plain view). It resembles the interconnecting columnar grains and results in a high roughness.

Fig. A4.10 – Topography of 3:2 ratio nano-multilayers (90Cu/W/60Sn/W)x10: (a) in as-deposited state, AFM tapping (5 μm x 5 μm); (b) upon the in-situ HT-XRD thermal exposure at maximum of 450 °C SEM plain view; SE, 20 kV.

The cross-section of as-deposited state is seen in Fig. A4.11. The multilayer nature of the sample is disturbed by the highly wavy character of the deposited layers. Initial Cu layer at the substrate is however flat. The grains are uniform and fine, in sizes not exceeding 100 nm. The EDS analysis shows clearly the W positions. More Cu-rich or Sn-rich regions are visible, but the layers seem to overlap each other. It might be reasoned in the sample roughness.
Fig. A4.11 – Cross-section of nano-multilayer (90Cu/W/60Sn/W)\textsuperscript{x10}; TEM, BF, DF, and EDS mapping at 200 kV (colour coding Sn – green, Cu – blue, W – red).

Phase identification was performed upon in-situ heating with XRD in grazing incident setup. The experimental results for 90Cu/W/60Sn/W during in-situ heating up to 300 °C are presented in Fig. A4.12. The position of main Cu 111 and possible IMC phases – Cu\textsubscript{6}Sn\textsubscript{5}, Cu\textsubscript{10}Sn\textsubscript{3} and Cu\textsubscript{3}Sn are shown.
Fig. A4.12 – Set of chosen normalised diffractograms at 30°-300 °C for (90Cu/W/60Sn/W)x10: GI-XRD, theta-2theta (20-80°).

From room temperature up to 200 °C, the Cu₆Sn₅ and Cu are possible seen. At 200 °C it shifts into the position matching Cu₁₀Sn₃ reflex, also Cu₅Sn reflex appear.

Discussion and Conclusion

The nano-multilayers of Cu/W/Sn/in were analyzed to allow for the controlled initiation of the reactive interdiffusion between Cu and Sn in nano-multilayer configuration. The experimental results confirmed the separation of the Cu/Sn with W interlayer. For thin (up to 50 nm Cu-Sn bi-layer thickness) the multi-layer nature of the films was achieved. The roughness caused by the layer growth mechanism distorted the multi-layer geometry of the sample with 150 nm thick Cu-Sn bi-layer.

Unfortunately, the control of the reaction was not achieved through the incorporation of W barrier. The phases in the samples could not be clearly identified. Even for main peak position and its evolution the analyses did not provide a clear conclusion.

The W is not observed during XRD identification, except for the thinnest sample of 15 nm Cu-Sn bi-layer due to overall Cu-Sn volume. For the sample with 15 nm Cu-Sn bi-layer a possible interaction of Cu or Sn with W might happen. At this length scale, the W atoms could affect Cu or Sn lattice. For the 50 nm Cu-Sn bi-layer thick sample it could be speculated that upon 200 °C the Cu₁₀Sn₃ forms. A typical phase formation during soldering involves formation of Cu₆Sn₅ at the initial solid-solid interface of Cu/Sn. With heating above 60 °C, the Cu₅Sn starts nu-
cleating and growing at the Cu/Cu₆Sn₅ interface. For the sample with 150 nm thick Cu-Sn bi-layer Cu₆Sn₅ and Cu could be statistically identified. At 200 °C the Cu₁₀Sn₃ and Cu₃Sn peaks were seen.

The separation of the Cu/Sn layers with W thin film was achieved. The control of the reaction between Cu and Sn in nano-multilayer geometry, however, could not be assured and the driving forces for the reaction were therefore not analysed.