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The effect of platinum contact metallization on Cu/Sn bonding

Abstract

In this work, formation and evolution of microstructures in CuSn/Pt bonding were investigated after 320 °C reflow process as well as after high temperature storage test at 150 °C. Sputtered thin film platinum on silicon wafer and high purity platinum sheet were applied as contact metallizations for electroplated copper-tin based bonding metallurgy. As bonded microstructure showed PtSn₄ intermetallic compound growth at the Pt/Sn interface, and both Cu₆Sn₅ and Cu₃Sn phases formed at the Cu/Sn interface. Both hexagonal and monoclinic Cu₆Sn₅ were found to coexist after 1000 h high temperature storage test. Platinum was discovered to dissolve into the Cu₆Sn₅ phase during soldering process and form (Cu,Pt)₆Sn₅ intermetallic compound exhibiting hexagonal allotropy. Meanwhile, under annealing, monoclinic Cu₆Sn₅ phase layer without platinum was observed to form between (Cu,Pt)₆Sn₅ grains and tin. Thermodynamic analysis was performed in order to reason the effects of Pt on the phase equilibria and phase stabilities. Results show that platinum has a significant impact on the stability of hexagonal Cu₆Sn₅.

Keywords: Contact metallization, bonding, microstructure, thermodynamics
1. Introduction

The continuous growth in performance of electronics is based on enhancing the integration level with the “More-than-Moore” approach [1,2]. This platform can be applied to functional units such as processor, memory, sensors and actuators by wafer-to-wafer bonding and using through-silicon vias (TSVs). Metal bonding is a promising method for connecting wafers having different types of functions as well as in wafer-level packaging of IC and microelectromechanical systems (MEMS) [3–5]. As interconnect dimensions reduce drastically, the result is that a large fraction of the bond microstructure consists only of intermetallic compounds (IMCs) [3,6,7]. At this scale, the interfacial reactions play a significant role in the wafer bonding process as well as under subsequent assembly processes, which finally has direct impact on the bond performance. Thus, understanding the growth of IMCs together with microstructural properties is crucial for designing reliable devices [8–11]. Overall, the selection of materials and processing conditions will have a major influence on the performance of the advanced devices.

The copper-tin metallurgy is commonly utilized for interconnections due its mature manufacturing processes and experience. It is very suitable solution for several substrates, however, when considering stable contact metallization on the complex MEMS device wafer or integrated circuit (IC) wafer, platinum is a possible candidate as it is CMOS-compatible, does not oxidize and it reacts slower than gold, silver or palladium with liquid tin; yet exhibiting sufficient wetting performance [12,13]. Platinum also dissolves into liquid tin slower than nickel [12], the typical diffusion barrier utilized in Cu/Sn soldering, thus platinum could be utilized without additional buffer layer. As a result, process integration is streamlined when several features required from the contact metallization can be combined into one layer. In addition, platinum is biocompatible, which makes it extremely suitable for biomedical applications such as implantable devices, sensing electrodes, neuromodulators and microfluidic chips [14–17].

However, there is a limited amount of experimental data in the literature about interfacial reactions in CuSn/Pt system having μ-bump dimensions (<10 μm thick metal layers). Wang et al. studied the cross-interaction between copper and platinum sides having 150 μm thick tin solder in between bulk substrates,
and reflowed the stack different periods from 10 s up to 1 h [18]. Solubility of the platinum into the opposite side Cu-Sn intermetallic compounds was not observed, which is contradictory to results presented by Amagai [19] who reported dissolution of platinum into the Cu$_6$Sn$_5$ phase. On the other hand, in several publications, it has been shown that third element can stabilize the high temperature hexagonal (η) crystal structure of the Cu$_6$Sn$_5$ phase by preventing the polymorphic transformation to monoclinic (η'). For example, the effect of Ni [20–31], Au [20,27,32], Co [27,29,30,33,34], Fe [28,29,33,34], Pt [19,27], Pd [35,36], Zn [20,32] and In [32,37], to the Cu$_6$Sn$_5$ phase has been investigated extensively. Especially nickel has exhibited interesting results regarding the Cu-Sn interfacial microstructure and particularly the Cu$_6$Sn$_5$ phase [26,28,29,31]. It has been confirmed in several publications [25,26,32,38,39] that as little as 1 at-% of nickel in the Cu$_6$Sn$_5$ phase stabilizes the η-Cu$_6$Sn$_5$. Reported benefits of having the η-Cu$_6$Sn$_5$ present in the interconnection are reduced thermal expansion, increased elastic modulus and hardness as well as improved creep properties [19,21,38,40–42]. In addition, stresses related to polymorphic transformation due to volumetric difference of the hexagonal and monoclinic allotropes are avoided [38], which can inhibit cracking of the intermetallic compounds. In order to apply platinum as a contact metallization, it is highly important to examine the formation of the bonding microstructure and it's evolution under annealing as well as possible interaction to Cu/Sn IMCs as the thermodynamic description of Cu-Pt-Sn ternary system is not available in the literature.

In this paper sputtered platinum is utilized as a contact metallization layer for electroplated Cu/Sn metallization. An adhesion layer for Pt was selected to be titanium in this study, as it is commonly used in the CMOS/MEMS industry [13]. In addition, the Cu/Sn stack is also soldered to bulk platinum (unlimited Pt available) in order to study the thermodynamic equilibria of the Cu-Pt-Sn system. These results are compared to the thin film platinum samples focusing on the microstructural evolution under a high temperature storage (HTS) test. As there is no Cu-Pt-Sn ternary system description available in the literature, the calculation of phase diagrams using the CALPHAD method was utilized to provide preliminary isothermal and vertical sections.

2. Materials & Methods

A 40 nm thick TiW adhesion layer and a 500 nm thick gold seed layer were sputtered on thermally oxidized (300 nm SiO$_2$) silicon wafer. 5 µm of copper was electroplated utilizing NB Semiplate Cu 100 bath, followed by 7 µm of electroplated tin using NB Semiplate Sn 100 solution from NB technologies. Platinum was utilized as a contact metallization two ways: 1) as a sputtered layer on top of a 40 nm thick
Ti adhesion layer on thermally oxidized silicon wafers simulating realistic wafer-level metallization for bonding and 2) as a 100 µm thick bulk film (99.99% Goodfellow Inc) in order to study the reactions between the copper-tin metal stack and platinum. Both Cu/Sn and Ti/Pt metallized wafers were diced to 5x5 mm pieces. The samples were soldered in air muffle furnace at 320 °C for 100 s, 500 s and 2500 s by utilizing flux (Weller T0051383199), and air cooled to room temperature. The bonding procedures regarding time and temperature were selected to mimic wafer-level bonding conditions utilized for Au-Sn and Cu-Sn bonds [4,5,8,10,43–48]. The high temperature storage (HTS) aging test at 150°C was conducted with a Heraeus Instruments oven for 500 and 1000 hours. For the microstructural analysis, samples were cross-sectioned with standard metallographic methods. JEOL JSM-6330F field emission scanning electron microscope (SEM) with back-scattered electrons detector (BSE) and Oxford Instruments INCA X-sight energy-dispersive X-ray spectroscopy (EDX) equipment were used for the detailed microstructural analysis. The composition of phases was determined by averaging measurements from a minimum of 5 different locations with EDX.

An electron-transparent lamella from the top die side (i.e. from initial Cu/Sn interface) was prepared using an in-situ lift-out process with the using the dual-beam (SEM-FIB) FEI Helios NanoLab 600. Scanning transmission electron microscopy (STEM) micrographs, select area diffraction patterns (SADP) and EDX maps were collected using the JEOL-2800 transmission electron microscope (TEM) operated at 200 kV. The elemental mapping was made with a JEOL ultrafast silicon drift detector (SDD) with a large solid collection angle and a detection area of 100 mm².

Thermodynamic modeling

**Fig 1.** Schematic presentation of samples
In order to compose the thermodynamic description of the Cu-Pt-Sn system in this work, binary parameters were directly taken from the only thermodynamic description of Cu-Pt [49], and the latest updated assessments of Cu-Sn [50] and Pt-Sn [51]. Therefore, most of the original references evaluated in [50] and [51] are not duplicated here.

The lattice stability of the element \( i \) \((i = \text{Cu}, \text{Pt and Sn})\), referred to the enthalpy of its stable state at 298.15 K and 1 bar, \( H_i^{\text{SER}} \), is recommended by Scientific Group Thermodata Europe (SGTE) [52]. For details of analytical expressions of Gibbs energies and thermodynamic models of phases in binary systems, the reader may refer to descriptions in [49–51], here only the phase described in this work is briefly presented.

In order to include the effect of dissolved platinum, both \( \eta \)-Cu\(_6\)Sn\(_5\) and PtSn phases have the prototype of NiAs structure [50,51]. For the \( \eta \)-Cu\(_6\)Sn\(_5\) phase, it was reported that the Wykoff positions 2a and 2c were occupied by 100\%Cu and 100\%Sn, and the excess Cu atoms would occupy the 2d site [53]. In the PtSn crystal structure, the Pt and Sn atoms occupied the 2a and 2c sites respectively [54]. Consequently, the two phases were described with the \((\text{Cu},\text{Pt})_1:(\text{Cu},\text{Va})_1:\text{Sn}_1\) model, as was recommended for other NiAs or Ni2In prototype phases by Kroupa [55]. The molar Gibbs energy was expressed by following equation.

\[
G^{(\text{Cu},\text{Pt})_1:(\text{Cu},\text{Va})_1:\text{Sn}_1} = \sum a \sum b Y_a Y_b G_{a,b; \text{Sn}}^{(\text{Cu},\text{Pt})_1:(\text{Cu},\text{Va})_1:\text{Sn}_1} + RT(Y_{\text{Cu}}^l \ln Y_{\text{Cu}}^l + Y_{\text{Pt}}^l \ln Y_{\text{Pt}}^l) \\
+ RT(Y_{\text{Cu}}^l \ln Y_{\text{Cu}}^l + Y_{\text{Va}}^l \ln Y_{\text{Va}}^l) + Y_{\text{Cu}}^l Y_{\text{Cu}}^l Y_{\text{Va}}^l \left( \sum_{j=0,1} Y_{\text{Cu},(\text{Cu},\text{Va})_1:\text{Sn}_1}^{(\text{Cu},\text{Pt})_1:(\text{Cu},\text{Va})_1:\text{Sn}_1} \left( Y_{\text{Cu}} - Y_{\text{Va}} \right)^j \right) \\
+ Y_{\text{Pt}}^l Y_{\text{Pt}}^l Y_{\text{Va}}^l \left( \sum_{j=0,1} Y_{\text{Cu},(\text{Cu},\text{Pt})_1:(\text{Cu},\text{Va})_1:\text{Sn}_1}^{(\text{Cu},\text{Pt})_1:(\text{Cu},\text{Va})_1:\text{Sn}_1} \left( Y_{\text{Cu}} - Y_{\text{Pt}} \right)^j \right) \quad (1)
\]

In Eq. (1), ‘a’ and ‘b’ refer to elements in the first and second sublattice sites, respectively. The \( Y \) terms are the site fractions of each constituent on relevant sublattice. \( R \) is the ideal gas constant and \( T \) is the temperature (in Kelvin). The \( L \) terms are the interaction energies between components on one sublattice (separated by a comma) when other sublattices are completely occupied by one of their components (separated by a colon). The binary parameters related to Cu-Sn and Pt-Sn were cited from the literature.
[50,51], and the rest were evaluated in the present assessment to reproduce the solubility of Pt in η-
Cu₆Sn₅ phase at 320 °C and 150 °C.

3. Results and discussion

During the bonding processes, both Cu and Pt dissolve into liquid tin and form IMCs to the Cu/Sn
and Pt/Sn interfaces. As can be seen from Fig. 2a-b and 3a-b, at the copper side of the bond, both Cu₆Sn₅
and Cu₃Sn phases were observed after soldering, and layer thicknesses were proportional to the soldering
time (see Table 1). Platinum was detected in the Cu₆Sn₅ phase within all sample groups. Based on the
SEM-EDX analysis (see Table 1), after 100 s of soldering, the platinum content in the Cu₆Sn₅ phase was
~2 at-%; and with 500 s reflow time ~3 at-%, correspondingly. Thus, this phase was interpreted as
(Cu,Pt)₆Sn₅. Thin film samples reflowed for 2500 s exhibited a microstructure consisting of mainly the
(Cu,Pt)₆Sn₅ phase (see Fig. 4a), which had platinum solubility of ~5 at-%. Platinum was not detected in
the Cu₃Sn phase in any of the samples. However, in the Cu₃Sn phase, voiding was observed, which
arises from the combination of electroplating process and chemistry utilized as well as Kirkendall effect
[7,56–61]. The 2500 s bulk platinum samples failed, as reactions had continued to the extent that copper
had reacted completely and gold seed layer had started to participate to reactions. Thus, the samples were
excluded from the further analysis.
Fig. 2. On the left column, the thin film Pt substrate samples and on the right column, the bulk Pt substrate samples with 100 s soldering time. A) and b) show the as bonded microstructure; c) and d) after 500 h annealing at 150 °C and e) and f) after 1000 h annealing at 150 °C. Red dashed line separates the \((\text{Cu},\text{Pt})_5\text{Sn}_5\) and \(\text{Cu}_6\text{Sn}_5\) phases.
Fig. 3. On the left column, the thin film Pt substrate samples and on the right column, the bulk Pt substrate samples with 500 s soldering time. A) and b) show the as bonded microstructure; c) and d) after 500 h annealing at 150 °C and e) and f) after 1000 h annealing at 150 °C. Red dashed line separates the (Cu,Pt)_6Sn_5 and Cu_6Sn_5 phases.
Fig. 4. 2500 s soldered thin film samples a) as bonded and b) 1000 h annealed.

Table 1. Compositions of the observed phases based on SEM-EDX analysis

<table>
<thead>
<tr>
<th>IMC</th>
<th>Composition (at-%)</th>
<th>Thickness (100 s soldering time)</th>
<th>Thickness (500 s soldering time)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As bonded</td>
<td>1000h HTS</td>
<td>As bonded</td>
</tr>
<tr>
<td>PtSn₄</td>
<td>Cu: &lt;1 Pt: &lt;18 Sn: 81</td>
<td>Cu: &lt;1 Pt: 18 Sn: 82</td>
<td>TF 0.4±0.1</td>
</tr>
<tr>
<td></td>
<td>100s Cu: 51 Pt: 2 Sn: 47</td>
<td>100s Cu: 51 Pt: 2 Sn: 47</td>
<td>2.0±1.1</td>
</tr>
<tr>
<td></td>
<td>500s Cu: 50 Pt: 3 Sn: 47</td>
<td>500s Cu: 51 Pt: 2 Sn: 47</td>
<td>1.7±0.6</td>
</tr>
<tr>
<td></td>
<td>2500s Cu: 50 Pt: 5 Sn: 48</td>
<td>2500s Cu: 48 Pt: 4 Sn: 48</td>
<td>1.2±0.7</td>
</tr>
<tr>
<td>Cu₆Sn₅</td>
<td>- Cu: 52 Pt: 0 Sn: 48</td>
<td>-</td>
<td>TF 1.0±0.1</td>
</tr>
<tr>
<td>Cu₅Sn</td>
<td>Cu: 75 Pt: 0 Sn: 25</td>
<td>Cu: 75 Pt: 0 Sn: 25</td>
<td>TF 0.3±0.1</td>
</tr>
</tbody>
</table>
As shown in Figure 2a-b and 3a-b, platinum reacted with the tin during soldering, and formed the PtSn₄ phase within both thin film and bulk Pt samples. The PtSn₄ phase was thicker with bulk platinum samples, and some spalling of the PtSn₄ grains was observed into the tin during soldering. The amount of copper in the PtSn₄ phase was <1 at-% based on the EDX analysis i.e. below the detection limit of the equipment. Within the thin film samples, remaining thin layer of pure platinum was still observed after 100 s and 500 s soldering times. The situation after 2500 s soldering time differed drastically compared to shorter reflow times: the platinum was completely consumed in thin film samples, and large PtSn₄ grains were observed in local equilibrium with Cu-Sn IMCs, as presented in Fig. 4a. In addition, the titanium adhesion layer had reacted with tin and dissolved copper, and formed small separate grains at the substrate interface.

The thickness of the (Cu,Pt)₆Sn₅ phase did not change significantly during annealing. Instead, an additional Cu₆Sn₅ phase layer grew on top of the original (Cu,Pt)₆Sn₅ grains that were formed in the reflow as shown in figs 2c-f and 3c-f. The interface between these two phases is highlighted with red dashed lines and a minor contrast difference in back-scatter electron images between these two phases can be perceived. Platinum was not detected with the SEM-EDX in this Cu₆Sn₅ phase. Meanwhile, the Cu₃Sn phase grew thicker within all sample groups, however, growth rate differed between thin film and bulk samples. In bulk samples, surplus of platinum atoms for the Pt-Sn reactions was assumed to decrease Sn diffusion towards copper, and thus, the Cu₃Sn layer was assumed to be thinner.

During annealing, the platinum continued reacting with the tin and the PtSn₄ phase grew thicker. The sputtered Pt layer was consumed completely during the first 500 hours of annealing in all thin film samples. Other Pt-Sn IMCs were not detected in any of the samples even after 1000 h annealing, which is in line with the results presented by Yang et al. [12]. Platinum was not detected in the tin after annealing, and the copper solubility into Sn was at the detection limits of EDX (~1 at-%). These observations correlate well with the thermodynamic description of the Pt-Sn and Cu-Sn systems [50,51]. Reactions on the platinum side, i.e. formation of the PtSn₄ phase, is similar what has been reported in the literature both in soldering and under annealing [12,18,62]. As there was excess of platinum in the bulk substrate samples, the PtSn₄ layer was thicker (and respectively, the tin was consumed more) both after soldering and annealing. As platinum was found to dissolve into the (Cu,Pt)₆Sn₅ grains at the opposite Cu/Sn side and not into the Cu₆Sn₅ layer that formed during annealing, a STEM-EDX analyses were performed in order to study these phases more in detail.
3.1. STEM-EDX analyses of (Cu,Pt)$_6$Sn$_5$ and Cu$_6$Sn$_5$ phases

To confirm the SEM-EDX findings, STEM-EDX analyses of the copper side were undertaken from 1000h annealed sample that was originally soldered for 500 s. Figure 5 shows the results of these analyses, and illustrates clearly two distinct Cu$_6$Sn$_5$ grain compositions. The (Cu,Pt)$_6$Sn$_5$ grains located next the Cu$_3$Sn appear to have a significantly higher concentration of Pt when compared to the Cu$_6$Sn$_5$ layer formed during annealing.

![Figure 5](image)

**Fig. 5.** STEM-EDX analysis of Pt rich (Cu,Pt)$_6$Sn$_5$ grains with the boundaries between Pt-rich and Pt-absent Cu$_6$Sn$_5$ grains indicated with dashed lines, (a) BF micrograph, -EDX maps of (b) Cu, (c) Sn and (d) Pt.

To understand the difference between the dissimilar Cu$_6$Sn$_5$ grains, a select area diffraction pattern (SADP) analysis and diffraction simulation was undertaken in order to study the crystal structures. The results of the SADP indexing can be seen from figure 6. SADP at three zone-axes (ZA) were taken from
both the Pt-rich and Pt-absent Cu₆Sn₅ grains. Each ZA contains a common reflection identified along the Kikuchi lines during imaging. In addition, the lamella tilt angles for each ZA were recorded. The diffraction simulation correlated the three lamella tilt angles, reflections and reflection angles to match the correct ZA. Results from the diffraction simulation and SADP fitting showed that the grains containing Pt were hexagonal η-Cu₆Sn₅, whereas the grains without Pt were the standard low temperature monoclinic η'-Cu₆Sn₅. It appears that the Pt stabilises the high temperature hexagonal form of the Cu₆Sn₅ at room temperature.

**Fig 6.** SADP analysis of the crystal structure of the Pt-rich and Pt-absent Cu₆Sn₅ grains. Subfigure (a) is a STEM-BF micrograph of the Cu bonded side, with the SADP regions indicated and the phase boundaries highlighted by the red dashed line and the blue dashed line separating the η-(Cu,Pt)₆Sn₅ and Cu₆Sn₅ grains. Sub figures (b) - (c) are the SADP of the hexagonal η-(Cu,Pt)₆Sn₅ grain and (d) – (e) are the SADP of the monoclinic η'-Cu₆Sn₅ grain from two zone-axes.

Based on the microstructural and STEM-EDX analyses at Cu/Sn interface, a following phase formation sequence regarding η and η' phases can be concluded. First, when tin melts, both copper and platinum dissolve rapidly into liquid. Second, after supersaturation of the liquid tin near the original interface, the heterogeneous nucleation occurs and platinum exhibits cross-interaction to IMC formation at the Cu/Sn
interface (i.e. formation of $\eta$-(Cu,Pt)$_6$Sn$_5$). Third, these grains grow due to ripening flux mechanism and to the detriment of consumption of smaller grains. Last, under annealing, the platinum diffusion through solid tin is significantly slower (in practice insignificant as Pt is reacting with the tin and forms PtSn$_4$), and does not participate into formation of monoclinic Cu$_6$Sn$_5$. Meanwhile, copper diffuses both through the $\eta$-(Cu,Pt)$_6$Sn$_5$ formed during soldering, and especially through the grain boundaries. Due to the higher flux rate through grain boundaries, the $\eta'$.Cu$_6$Sn$_5$ forms first between and then on top of (Cu,Pt)$_6$Sn$_5$ grains, which can be seen in Fig 2c-f and 3c-f. In the next section, it is shown with thermodynamic analysis that hexagonal (Cu,Pt)$_6$Sn$_5$ is not in thermodynamic equilibrium with $\beta$-tin at 150 °C, and monoclinic $\eta'$-Cu$_6$Sn$_5$ should form in between.

3.2 The effect of platinum to the crystal structure of the Cu$_6$Sn$_5$ phase

As was shown, the platinum dissolves into the Cu$_6$Sn$_5$ phase, exhibiting similar phenomenon as Ni, Sb, Au, In and Zn [21,27,38,39,63–66], and based on the STEM analysis, stabilises the high temperature hexagonal ($\eta$) crystal structure. Previously Amagai [19] reported that alloying Sn with Pt nanoparticles and reflowing it on a copper substrate results Cu$_6$Sn$_5$ with 3.8 wt-% solubility of Pt. Meanwhile, Wang et. al. [18] did not detect any platinum in the Cu$_6$Sn$_5$ phase when Cu/Sn/Pt stack was reflowed even with extended durations. However, they had a thicker tin layer (150 µm) between copper and platinum sheets, which can explain the difference in results. The hexagonal ($\eta$) – monoclinic ($\eta'$) change has been previously determined to occur at 186 °C [27,66,67], but recent studies have shown that this transition temperature is in a range between 180 °C and 220 °C [21,38,63,64]. On the other hand, as low as 1 at-% of Ni in the Cu$_6$Sn$_5$ phase is sufficient to stabilize the high temperature hexagonal crystal form [21,38,39,63,64] to low temperatures, and even pure Cu$_6$Sn$_5$ can remain in hexagonal form depending on the cooling rate as kinetic requisites for the transformation are limited [27,37,38,64,66]. Nickel and gold [20,23,39] are known to replace copper atoms in the $\eta$-Cu$_6$Sn$_5$ unit cell, while Zn and In are substitutes for Sn [20,38]. The stabilization effect of nickel has been more pronounced, probably due to difference in atom size when compared to Au, and thus, the induced stress to surrounding atoms is different [22,25,67]. Several time-temperature-transformation (TTT) curves of the hexagonal to monoclinic transformation have been reported, and highlighted that factors such as cooling rate from bonding temperature and possible solid-state high temperature annealing have significant impact on the kinetics [15], [19], [21], [22], [24]–[26].
In order to study the effect of platinum in the Cu₆Sn₅ phase more in detail, the preliminary thermodynamic analysis was performed for the Cu-Pt-Sn system. The descriptions of these three binary systems were combined and the models for the observed phases were adapted in order to describe the detected solubility of the third element especially in the hexagonal \( \eta \)-Cu₆Sn₅. The parameters used to describe the solubility of the Pt element in the \( \eta \)-Cu₆Sn₅ and \( \eta' \)-Cu₆Sn₅ phases, were adjusted by progressively taking into account the experimentally determined phase equilibria and composition ranges. At each step of the evaluation, a systematic comparison has been done between all available experimental results and the calculated one. The evaluated thermodynamic parameters obtained in the present work are listed in Table 2.

**Table 2.** Thermodynamic parameters assessed in this work. Values are in SI units. Parameters of sub-binary systems of Cu-Pt-Sn were directly cited from the literature, i.e. Cu-Sn from [50], Cu-Pt from [49], and Pt-Sn from [51]. And data for pure elements are taken from SGTE [52].

<table>
<thead>
<tr>
<th>Defined functions, and phases</th>
<th>Parameters obtained in this work</th>
</tr>
</thead>
</table>
| NiAs (representing \( \eta \)-Cu₆Sn₅ and PtSn): \((\text{Cu,Pt})_1:(\text{Cu,Va})_1:\text{Sn}_1\) | \[ G_{\text{NiAs}}^{\text{Pt:Pt:Sn}} = +5000 + 2 \ast \text{GHSERTPT} + \text{GHSERSN} \]  
| \[ G_{\text{NiAs}}^{\text{Pt:Cu:Sn}} = +15000 + \text{GHSERCU} + \text{GHSERTPT} + \text{GHSERSN} \]  
| \[ G_{\text{NiAs}}^{\text{Cu:Pt:Sn}} = +15000 + \text{GHSERCU} + \text{GHSERTPT} + \text{GHSERSN} \]  
| 0 \[ \Gamma_{(\text{Cu,Pt}):\text{Cu}:\text{Sn}} = -100000 \]  
| 1 \[ \Gamma_{(\text{Cu,Pt}):\text{Cu}:\text{Sn}} = -80000 \]  |

Isothermal sections optimized based on the experimental data determined in this work at 150 °C as well as at 320 °C are presented in Fig. 7. In Fig 7a, the complete isothermal section at 150 °C is presented. In order to visualize the phase equilibria observed in the microstructures, enlargement from Sn rich corner at 320 °C and 150 °C is presented in Fig. 7b and 7c, respectively. A schematic presentation from the Cu₆Sn₅ region is in Fig.7d, where one can observe that \( \eta \)-(Cu,Pt)₆Sn₅ phase in equilibria with Cu₃Sn, \( \eta' \)-Cu₆Sn₅ and PtSn₄ phases. Thus, isothermal section at 150 °C explains the monoclinic \( \eta' \)-Cu₆Sn₅ phase formation in between the \( \beta \)-Sn and \( \eta \)-(Cu,Pt)₆Sn₅ phases under annealing at 150 °C, as \( \eta' \)-Cu₆Sn₅ is in equilibria with \( \eta \)-(Cu,Pt)₆Sn₅, \( \beta \)-Sn and PtSn₄. On the other hand, as shown in Fig 7b, reactions and phase sequence observed after bonding can be reasoned as the hexagonal (Cu,Pt)₆Sn₅ is in equilibrium with Cu₃Sn, \( \beta \)-Sn and PtSn₄ phases at soldering temperature of 320 °C.
Fig. 7 The calculated isothermal section of Cu-Pt-Sn at a) 150 °C and b) 320 °C, experimental data were superimposed on. C) Partial isothermal section at 150 °C showing the Sn rich part of the isothermal section in a). D) High magnification from the region around the Cu₆Sn₅ phase demonstrating the phase equilibria. Superimposed purple line indicates the direction of vertical section and Gibbs energy diagram shown in Figs. 9 and 10.

In order to explain the effect of dissolved platinum into the Cu₆Sn₅ phase, a vertical section from Cu₆Sn₅ with constant Sn concentration of 45 at.% along the purple line superimposed in Fig. 7, is presented in Fig. 8. As can be seen from this figure, the dissolved Pt decreases strongly the \( \eta \rightarrow \eta' \) transition temperature (see purple arrow in Fig 8.). Thermodynamic analysis indicates that (Cu,Pt)₆Sn₅ should
transform to monoclinic crystal structure at ~120 °C, which was not observed in the STEM analysis (performed ~1 month after the end of the annealing). Similar effect even with pure Cu-Sn binary system is commonly detected, as the transform does not occur within a reasonable time because of kinetic constraints [20,27,38,64,66].

Fig. 8 Partial vertical section along the dashed line shown in Fig. 8 from pure Cu₆Sn₅ towards hypothetical Pt₆Sn₅ i.e. constant Sn content.

Generally, platinum appears to stabilize high temperature hexagonal (η) crystal structure of the Cu₆Sn₅ phase similar as nickel. To compare this stabilization effect of platinum and nickel, the graph of Gibbs free energy as function of composition of the third element (i.e. a G-xi diagram) in the Cu₆Sn₅ phase was calculated and is presented in Fig. 9. A stronger stabilizing effect is obtained with platinum compared to
nickel. Authors would like to highlight, that the solubility of the nickel in the Cu₆Sn₅ phase is larger [24,26,28,38,68] than now observed with platinum, and thus, the overall stabilization effect can be higher with Ni than Pt. Meanwhile, it is plausible to assume that, as the crystal transformation η' -> η is sluggish in pure Cu-Sn system due to kinetics constrains, introducing a ternary element that further stabilizes the η'-phase (i.e. decreases the Gibbs free energy significantly), the transformation becomes even more obstructed. Thus, it is reasonable to observe both η- and η'-phases even after annealing. On the other hand, η to η' transformation may induce local stresses due to 2.15 % volumetric expansion (pure Cu₆Sn₅ without third elements) [22,32,38,40,42,67]. Therefore, stabilization of the high temperature hexagonal crystal structure can enhance the reliability of the joints by preventing the IMC cracking [27,38,39,64,66,69]. Hence, platinum provides to be a potential candidate as a contact metallization for Cu-Sn interconnections exhibiting similar characteristics as nickel in stabilizing the hexagonal crystal structure of the Cu₆Sn₅ phase.

Fig. 9 Gibbs energy diagram of the (Cu,Pt)₆Sn₅ at 150°C as a function of Pt (solid line) content through the vertical section shown in Fig. 9. The effect of dissolved Ni (dashed line) in (Cu,Ni)₆Sn₅ is superimposed based on the data from [68].
4. Conclusions

Viability of platinum as a contact metallization for Cu/Sn bonding metallization was studied in this paper. Platinum was observed to dissolve into the Cu₆Sn₅ phase formed at the Cu-Sn interface during soldering process and form (Cu,Pt)₆Sn₅ intermetallic compound. In addition, platinum was discovered to stabilize the high temperature hexagonal ($\eta$) crystal structure of the (Cu,Pt)₆Sn₅ phase to room temperature, and polymorphic transformation to low temperature monoclinic crystal structure was not observed even after 1000h high temperature storage test at 150 °C. On the other hand, platinum was not observed to dissolve into the Cu₆Sn₅ phase having the monoclinic crystal structure, which grows between the (Cu,Pt)₆Sn₅ grains and Sn during annealing. Meanwhile, copper was not observed to dissolve into the PtSn₄ phase formed at platinum metallization interface. Thermodynamic analysis was performed and isothermal section, vertical section and Gibbs energy diagram were presented. The stabilizing effect of platinum in the hexagonal Cu₆Sn₅ was discovered to be even more pronounced than in the case of nickel that has been investigated extensively in the literature. Due to the fact that IMCs in the high density interconnections are large fraction of the bump, it is highly important to understand the microstructure after bonding as well as reactions taking place under operation. Altogether, platinum is a potential contact metallization for 3D-integration of electronics and sensors, where only limited selection of elements can be utilized in e.g. biomedical applications, MEMS or IC-wafer processing.

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