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Investigation of the microstructural evolution and detachment of Co in contact with Cu–Sn electroplated silicon chips during solid-liquid interdiffusion bonding

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Abstract

Solid-liquid interdiffusion (SLID) bonding is one of the most promising novel methods for micro-(opto-)electromechanical system (MEMS/MOEMS) wafer-level packaging. However, the current SLID bonding solutions require the use of an electrochemical deposition method for MEMS/MOEMS wafers as well, which significantly complicates the process integration options. Hence, this work proposes Co as a potential option for compatible contact metallization on MEMS/MOEMS wafers to utilize mature Cu–Sn SLID bonding. The focus of this study is on gaining a fundamental understanding of the microstructural formation and evolution of Co substrates in contact with Cu–Sn electroplated silicon wafers and identifying possible failures of joints during bonding, which are prerequisites for guaranteeing devices’ manufacturability, functionality, and long-term reliability. The effect of bonding time and temperature on the microstructural evolution and phase formation of Co substrates in contact with Cu–Sn electroplated silicon chips was investigated. Moreover, a phase diagram of the Co–Cu–Sn ternary system was thermodynamically evaluated based on experimental data. Samples were successfully bonded at 250 °C for 1500 and 2000 s and at 280 °C for 1000 s. The main interfacial intermetallic compounds were identified as (Cu,Co)6Sn5, Cu3Sn, and (Co,Cu)Sn3. Co stabilized the high-temperature hexagonal (η) Cu6Sn5 phase down to room temperature. Bond detachment was observed when applying either a higher bonding temperature or a longer bonding time. Two critical factors that cause detachment during bonding were recognized: first, a change in thermodynamic equilibrium when exceeding the maximum allowed Co content in Cu6Sn5 formed adjacent to the CoSn3 phase and a discontinuous change in the Co content in the Cu6Sn5 grown on the Cu and Co sides; second, stress exerted due to the rapid growth of (Co,Cu)Sn3 between the Co substrate and (Cu,Co)6Sn5. Therefore, achieving successful bonding in the Co–Sn–Cu SLID system requires governing the amount of dissolved Co atoms in liquid Sn and the CoSn3 formation, both of which can be achieved by manipulating the relative thickness of the Co, Cu, and Sn layers. The observations and calculations in this work show that a prerequisite for obtaining successful bonding in the Co–Sn–Cu SLID system at 250 °C is a Co-to–Sn thickness ratio of 0.04 or less.

1. Introduction

The unique nature of functional micro-(opto-)electromechanical systems (MEMS/MOEMS), such as sensors and actuators, calls for specific prerequisites: protecting fragile movable parts, providing a specific ambient, and making electrical paths to interact with the environment. In this regard, a combination of wafer-level bonding and through-silicon vias technology has attracted considerable attention [1,2]. A wide range of wafer-level bonding has been applied in electronic manufacturing, including direct, anodic, glass frit, adhesive, and metal bonding (such as eutectic and solid-liquid interdiffusion [SLID] bonding). Wafer bonding processes using SLID bonding have attracted considerable interest, as they can form high remelting temperature intermetallic compound (IMC) joints at relatively low bonding temperatures. Other advantages of SLID bonding are fine-pitch bonding, well-defined metallurgy, substantial reduction of the bonding footprint compared to other bonding methods, and high current density capabilities. The SLID process is commonly based on a binary system with a high-temperature and a low-temperature melting metal [3–7]. Among various SLID bonding
systems, such as Cu–Sn, Cu–In, Ag–Sn, Ag–In, Ni–Sn, Au–Sn, and Au–In. Cu–Sn-based metallurgy is one of the most popular material systems utilized in MEMS encapsulation and interconnection due to its low process temperature (250–350 °C), high thermal stability, and excellent mechanical reliability. Additionally, the manufacturing processes for Cu–Sn micro-joints are mature and easily available at a relatively low cost. Two main IMCs formed in Cu–Sn SLID bonding are Cu 3Sn and Cu 6Sn5, which have remelting temperatures of 676 and 415 °C, respectively [6–8]. The allotropic transformation from high-temperature hexagonal ƞ-Cu 6Sn5 to low-temperature monoclinic ƞ’-Cu 6Sn5 at a temperature of less than 186 °C and void formation due to the Cu3Sn phase formation deteriorate the mechanical properties of the joints [9–13]. Various metals, such as Ni, Au, In, and Zn, have been widely explored as the third elements for Cu–Sn SLID bonding systems to stabilize the high-temperature hexagonal ƞ-Cu6Sn5 phase. Furthermore, elements such as Zn and Ni can suppress the Cu3Sn phase formation and subsequently void formation [9,14–23].

Regarding the wafer-level packaging of MEMS devices, typical process integration challenges are related to the chemical/electrochemical plating processes for the SLID interconnection materials without negatively impacting the sensitive MEMS structures or vice versa. It is necessary to protect the sensitive MEMS structures from either the wet-chemistry or plated metals during the deposition processes. Nowadays, research is focusing on single contact metallization or metallization stacks that could be manufactured with PVD (Physical vapor deposition) or CVD (Chemical vapor deposition) methods on MEMS device wafers. These must be complementary metal-oxide-semiconductor (CMOS)/MEMS-compatible and chemically compatible with SLID bonding metallurgies, which are applied on the cap wafers. Rautiainen et al. explored the possibilities of CMOS-compatible Pt metallization for single-layer contact material for Cu–Sn SLID bonding utilized on MEMS device wafers and found that Pt dissolves in Cu6Sn5 and stabilizes high-temperature hexagonal ƞ-Cu6Sn5 down to room temperature. The presence of Pt also provides stable contact during aging [24]. However, like gold, platinum—as a noble metal—has a challenging etch process. Ni and Cu are widely used as contact metallization layers for soldering. However, the use of Ni and Cu for contact metallization for SLID bonding presents certain difficulties. For instance, Ni is challenging due to its fast oxidization [25], stresses exerted during thick layer sputtering, and the brittleness of the IMCs. Cu dissolves rapidly in Sn, and therefore a thick Cu layer is required.

Co is a promising metallization candidate for soldering joints due to its many favorable attributes, such as superior diffusion barrier capability, excellent thermal cycle fatigue, high electromigration resistance, acceptable wettability, and mechanical strength in solder joints [26–33]. Co substitutes the Cu atoms in Cu–Sn IMCs, promoting Cu6Sn5 phase formation, stabilizing the hexagonal Cu6Sn5 phase down to room temperature, refining the grain morphology, and suppressing the Cu3Sn phase formation and subsequent void formation [31,34–38].

IMCs formed in ternary or binary systems depend on the bonding conditions (bonding temperature and bonding time). For instance, a Co–Sn binary system has four stable phases at room temperature: Co3Sn, CoSn, CoSn2, and CoSn3. However, it is possible that only one or two phases are present in bonding areas, depending on factors such as bonding conditions, experimental setup, and additional elements [32,39]. Previous studies have examined various IMCs in the Cu–Sn–Co ternary system. Studying Cu–Sn–Co joints, Du et al. observed (Cu,Co)6Sn5, (Co,Cu)Sn, and (Co,Cu)Sn2 in the joint area, depending on the bonding temperature and time [38]. Because IMC properties have a substantial impact on the thermomechanical properties and reliability of SLID bonding, it is vital to understand
the type and thickness of IMCs formed in Co–Sn–Cu under various bonding conditions and optimize them to achieve highly reliable bonds.

Co can thus be considered a candidate for contact metallization in Cu–Sn SLID bonding on MEMS device wafers. However, before introducing a new metal for contact metallization in Cu–Sn SLID bonding, a comprehensive understanding of the interfacial reactions is of utmost importance. The IMCs evolving in the interfacial layer differ depending on factors such as varying thickness of the Cu and Sn layers and temperature. This work aimed to investigate the microstructural evolution of Co substrates in contact with 4-µm Sn/8-µm Cu electroplated silicon chips to explore the possibility of using Co for contact metallization for Cu–Sn SLID bonding on MEMS device wafers and to identify possible failures of joints during bonding.

2. Materials and methods

2.1. Specimen preparation

Co foil (purity: 99.99%, Goodfellow Ltd.) 1 mm in thickness was cut into pieces 1 × 1 cm in size. The pieces were mechanically ground to 2400 papers, cleaned with acetone, and air-dried before bonding. Fig. 1 shows an illustration of the fabrication steps. All samples were prepared on thermally oxidized (300-nm SiO2) 4" Si (<100> wafers). A 60-nm-thick Ti/W adhesion layer was sputtered on the wafer, followed by sputtering of a 100-nm-thick Cu seed layer. Cu (8 µm) was electroplated using an NB Semiplate Cu 100 bath (NB Technologies), followed by 4-µm electroplated Sn using an NB Semiplate Sn 100 solution (NB Technologies). Cu–Sn metallized wafers were cut into 5 × 5 mm pieces. Finally, the prepared chips in contact with Co foil pieces were placed in a relatively large metal holder. They were then soldered in an air muffle furnace under different bonding conditions using flux (Weller T0051383199) and air-cooled to room temperature. The temperature increases versus the time for set furnace state aging at 150 °C for 1000 h.

Three bonding conditions were applied:

1) A bonding temperature of 250 °C and bonding times ranging from 1500 to 3000 s
2) A bonding temperature range of 280–320 °C for 1000 s
3) A bonding temperature of 250 °C for 1500 s, followed by solid-state aging at 150 °C for 100 h.

The bonding time and temperature conditions were selected to mimic wafer-level bonding conditions for Cu–Sn bonds.

2.2. Microstructural analysis

A JSM-6330F field emission scanning electron microscope (SEM; JEOL Ltd.) with a backscattered electron (BSE) detector, an INCA X-sight energy-dispersive X-ray spectroscopy (EDX) system (Oxford Instruments), a JIB-4700F focused ion beam (FIB; JEOL Ltd.) with upper secondary electron (USE) imaging, and a SmartLab X-ray diffractometer (Rigaku) equipped with a 9-kW rotating Cu anode source and a 2D single-photon counting pixel detector (HyPix-3000) were used for detailed microstructural analysis. For cross-section analysis using SEM and EDX, samples were prepared using standard metallographic methods. The composition of phases was determined by averaging measurements from a minimum of five locations using EDX. A detached sample soldered at 250 °C for 3000 s was selected for examination using high-resolution X-ray diffraction (XRD) and two-dimensional XRD (2D-XRD). Data were collected in a 2θ range of 25–85°.

2.3. Thermodynamic calculation

The calculation of phase diagrams (CALPHAD) method was used to construct a phase diagram of the ternary Co–Cu–Sn system. The system was thermodynamically evaluated based on binary thermodynamic descriptions [39–41] and experimental investigations of the ternary phase equilibria in a previous study [42] in this work. The lattice stability of element i (i = Co, Cu, or Sn) refers to the enthalpy of its stable state at 298.15 K and 100 kPa, H_{SEP}, as recommended by Scientific Group Thermodata Europe [43]. Thermodynamic parameters of compounds in the binary systems were directly taken from relevant publications: Co–Cu according to Turchin and Agraval [39]; Co–Sn according to Jedlicková et al. [40], and Cu–Sn according to Dong et al. [41]. Regarding the ternary system, most binary compounds have the solubility of a third element, as reported by Chen et al. [42]. To describe the experimental observations, proper sublattice-site models were defined based on an analysis of the experimental results, as well as the crystal structure of the relevant compounds. For instance, stoichiometric binary compounds exhibiting the solubility of the third elements were treated as semi-binary compounds—for example, (Co,Cu)Sn in Cu and the (Cu,Co)Sn in Co. Binary compounds with NiAs prototype crystal structure—that is, CoSn2 HT and Cu3Sn, HT (HT: high temperature)—were treated as phase with a sublattice model of (Co,Cu,VS):1:(Co,Cu,VS):1:(Sn):1. There was also a ternary line compound—Co3Cu–Sn—in this ternary system, which was modeled as a stoichiometric compound. The thermodynamic parameters of the involved phases were evaluated accordingly. The obtained thermodynamic database can reproduce these experimentally determined phase equilibria.

3. Results

3.1. Growth of intermetallic phases between Co substrates and Cu-Sn electroplated silicon chips under various bonding conditions

The Cu–Sn–Co stacks were successfully bonded at 250 °C for 1500 and 2000 s and at 280 °C for 1000 s. Detachments occurred at 250 °C for 2500 s and at 300 and 320 °C for 1000 s Fig. 2 shows cross-sectional BSE images of Cu–Sn–Co sandwiched under various bonding conditions (250 °C for 1500–3000 s and 280–320 °C for 1000 s). EDX was used to identify the elemental compositions of the interfacial IMC layers. Three phases were identified in the bonding zone: (Cu,Co)xSn, Cu3Sn, and (Co,Cu)Sn2. Immediately after bonding, the (Co,Cu)xSn2 phase grew separately from both the Cu–Sn and Co–Sn interfaces, and a thin layer of Cu3Sn appeared between electroplated Cu and the (Cu,Co)xSn2 IMC. In contrast, (Co,Cu)Sn2 formed at higher temperatures and after longer bonding times, suggesting that its formation requires bonding at a higher temperature-time average. A comparison of the results of several samples suggested that the various bonding conditions provided similar microstructural evolution effects, the only difference being in the reaction kinetics. The Co content in the (Cu,Co)xSn2 layer was 2 at% on average on the Cu side and between 4 and 8 at% on the Co side, depending on the bonding temperature and time. With an increase in either the temperature or the time, the Co content in Cu3Sn increased. The dissolved Co content in (Cu,Co)xSn2 adjacent to (Co,Cu)Sn2 was considerably higher in detached samples (~12 at%) than in successfully bonded samples.

The fracture surfaces of the sample prepared at 250 °C for 3000 s were analyzed. Top-view BSE images are shown in Fig. 3. The phases on the surfaces of the Co and Cu sides were identified as (Cu,Co)xSn. Most (Cu,Co)xSn grains on the Cu side contained 2 at% of Co on average, while a few grains contained 5 at%. On the Co side, the Co content was 12 at% in most (Cu,Co)xSn grains and 5 at% in a few grains. As shown in Fig. 3, when the Co content in (Cu,Co)xSn increased, the grains became smaller and finer. This finding is in line
with previous investigations [37,44]. Moreover, the (Cu,Co) 6Sn5 grains with lower Co contents (2 and 5 at%) exhibited a faceted structure with a diameter between 2.4 and 5 µm and a length between 4 and 9 µm. However, the grains containing 12 at% of Co on the detached sample’s Co side had a significantly smaller size than those on the Cu side.

Fig. 4 shows a BSE image of an FIB polished sample (bonded at 250 °C for 2000 s) and a USE image from the cross-section area, shown with red arrows in the BSE image. The visible boundaries of (Cu,Co) 6Sn5 phase are indicated by dashed red lines in the USE image. The Co content in (Cu,Co) 6Sn5 increased from 2.4 to 8.1 at% across the reaction area from the Cu to the Co side. Sharp edges were visible in the Sn/(Cu,Co) 6Sn5 phase boundaries, especially on the Cu side, indicating a hexagonal crystal structure of (Cu,Co) 6Sn5. Morphology observations suggested that (Cu,Co) 6Sn5 formed on both the Cu and Co sides was faceted, with diameters between 2.1 and 4.6 µm.

3.2. Evolution of intermetallic phases between Co substrates and Cu–Sn electroplated silicon chips during solid-state aging

Cross-sectional BSE micrographs of the samples bonded at 250 °C for 1500 s before and after aging at 150 °C for 1000 h are illustrated in Fig. 5. As discussed in Section 3.1, during bonding at 250 °C for 1500 s, the only IMCs observed were a layer of (Cu,Co) 6Sn5, which

Fig. 2. Cross-sectional BSE SEM images of Cu-Sn-Co joints formed at (a) 280 °C, (b) 300 °C, and (c) 320 °C for 1000 s and at 250 °C for (d) 1500 s, (e) 2000 s, and (f) 3000 s.

Fig. 3. Top-view BSE image of a detached sample prepared at 250 °C for 3000 s (a) Cu side and (b) Co side.
grew on both the Cu and Co sides, and a thin layer of Cu$_3$Sn between Cu and (Cu,Co)$_6$Sn$_5$. No new phase was observed after annealing at 150 °C for 1000 h. The (Cu,Co)$_6$Sn$_5$ phase layers formed on the Cu and Co sides continued to grow and created an almost continuous vertical phase structure between the Co substrate and electroplated Cu on the silicon chip. Only a small amount of Sn remained on the Co side after long-time annealing. Notably, (Co,Cu)Sn$_3$ did not nucleate during the aging time.

3.3. Phase and crystal orientation identification using XRD and 2D-XRD

To better identify the IMCs formed at the bonding interface, XRD analysis was performed. Fig. 6 shows the XRD diffractograms of Co–Sn–Cu joints prepared at 250 °C for 3000 s before and after aging at 150 °C for 1000 h (examined from the top surface of the detached Cu and Co sides). Three IMCs were identified as hexagonal Cu$_6$Sn$_5$ and orthorhombic Cu$_3$Sn on the Cu side and hexagonal Cu$_6$Sn$_5$ and CoSn$_3$ on the Co side. It should be noted that CoSn$_3$ has two crystal structures: $\alpha$ and $\beta$. As distinguishing between these two crystal structures using XRD diffractograms is difficult, we did not identify the crystal structure of CoSn$_3$ IMCs formed at the bonding interface. The XRD results were in good agreement with the EDX analysis. Peaks related to the unreacted Cu and Si wafer were also identified. According to the XRD diffractograms, aging did not cause a phase transformation of Cu$_6$Sn$_5$ from a hexagonal crystal structure to a monoclinic crystal structure.

As Cu$_6$Sn$_5$ has various Co contents, it is essential to study the effect of Co on its crystal orientations, which can impact the thermomechanical properties of the joints. One way to identify the crystal orientations is to analyze wide-area diffraction space maps, on which 2D diffraction patterns are manipulated and interpreted. On a wide-area diffraction space map, the horizontal and vertical axes show a chi angle ($\chi$: diffraction vector tilt angle) and 2$\theta$, respectively. The diffraction maps indicate the direction of the measured crystallographic planes, revealing the preferential crystal orientation of a sample. In this work, samples were scanned in a chi angle range of −10–50°. Fig. 7 displays the wide-area diffraction maps of Co–Sn–Cu joints on the Cu and Co sides prepared at 250 °C.
temperature sensitive than Cu₆Sn₅ growth [41]. Furthermore, Wang et al. reported that CoSn₃ formation at the initial bonding stages was significantly suppressed when a Cu diffusion barrier deposited on the Cu substrate contacted SAC solder compared to pure Sn solder [38]. This suggests that Cu in solder delays the dissolution of Co atoms and, consequently, the formation of a CoSn₃ IMC. Once the Cu content near the Co layer decreased due to (Cu,Co)₆Sn₅ IMC formation, CoSn₃ became the dominant phase. The rapid formation of (Cu,Co)₆Sn₅ compared to (Co,Cu)Sn₃ is in line with Chen et al.'s conclusion that Cu diffusivity in Sn is considerably higher than Co diffusivity and that the maximum solubility of Co in liquid Sn is 0.04 wt%. Therefore, it can be concluded that the accumulation of Cu close to the Sn/Co interface inhibited Cu dissolution in Sn to form (Co,Cu)Sn₃, whose formation obviously required a significantly higher amount of dissolved Co than that of (Cu,Co)₆Sn₅. The formation of (Co,Cu)Sn₃ at the Co/Sn interface led to the consumption of Cu adjacent to the Co substrate. At the subsequent stages, Sn passed through (Cu,Co)₆Sn₅ and reacted with Co to form (Co,Cu)Sn₃, as shown in Fig. 8c and d.

Fig. 7. Wide-area diffraction maps of Co–Sn–Cu joints bonded at 250 °C for 3000 s. Top-view analysis of (a) the Cu side and (b) the Co side.

for 3000 s. The diffracted lines related to Cu₆Sn₅ are marked by a. Diffraction lines of the basal plane (0001), which are indicated by dotted white arrows, were not observed on the studied maps. Hence, it can be concluded that the crystals were orientated with their c-axis in the sample's in-plane direction. The results indicate that there was no noticeable crystal orientation difference between (Cu,Co)₆Sn₅, (Co,Cu)Sn₃, and (Cu,Co)₃Sn, depending on the bonding temperature and time. A schematic illustration of the elements' diffusion direction and IMC formation in the observed sequence based on the experimental observations is shown in Fig. 8. First, both Cu and Co dissolved rapidly in liquid Sn and moved in opposite directions. Subsequently, the (Cu,Co)₆Sn₅ IMC (layer I) nucleated and grew at both the Co/Sn and Cu/Sn interfaces (Fig. 8a). Next, a thin layer of Cu₆Sn₅ with negligible Co content (layer II) formed between Cu and (Cu,Co)₆Sn₅ (Fig. 8b). Meanwhile, Sn diffused through (Cu,Co)₆Sn₅ on the Co side, and consequently, (Co,Cu)Sn₃ (layer III) formed between Co and (Cu,Co)₆Sn₅ (Fig. 8c). The findings suggest that the (Co,Cu)Sn₃ IMC requires a higher bonding temperature and/or a longer bonding time to form than the (Cu,Co)₆Sn₅ IMC. According to Tian et al., CoSn₃ growth is more

4. Discussion

The experimental results show that the reaction products of the Co substrates in contact with the Cu–Sn electroplated silicon chips were (Cu,Co)₆Sn₅, (Co,Cu)Sn₃, and (Cu,Co)₃Sn, depending on the bonding temperature and time. A schematic illustration of the elements' diffusion direction and IMC formation in the observed sequence based on the experimental observations is shown in Fig. 8. First, both Cu and Co dissolved rapidly in liquid Sn and moved in opposite directions. Subsequently, the (Cu,Co)₆Sn₅ IMC (layer I) nucleated and grew at both the Co/Sn and Cu/Sn interfaces (Fig. 8a). Next, a thin layer of Cu₆Sn₅ with negligible Co content (layer II) formed between Cu and (Cu,Co)₆Sn₅ (Fig. 8b). Meanwhile, Sn diffused through (Cu,Co)₆Sn₅ on the Co side, and consequently, (Co,Cu)Sn₃ (layer III) formed between Co and (Cu,Co)₆Sn₅ (Fig. 8c). The findings suggest that the (Co,Cu)Sn₃ IMC requires a higher bonding temperature and/or a longer bonding time to form than the (Cu,Co)₆Sn₅ IMC. According to Tian et al., CoSn₃ growth is more

Based on the XRD results, (1) and (2) seem implausible, as (Cu,Co)₆Sn₅ on both sides was hexagonal and retained this structure after long-term aging. Therefore, no phase transformation occurred during cooling. Moreover, crystal orientation observations showed that (Cu,Co)₆Sn₅ growth on the Cu and Co sides had similar growth
characteristics and crystal orientations. Therefore, the other two possible reasons were investigated in detail.

4.1. Growth of IMCs and volumetric changes

The thicknesses and relative fractions of IMCs as functions of bonding time and temperature are shown in Fig. 9. With an increase in the temperature or time, the thickness of (Cu,Co) 6Sn 5 and (Co,Cu)Sn 3 formed on the Co side and the total thickness of the IMCs increased. The thickness of the (Co,Cu)Sn 3 IMC and the total IMC layer drastically increased at higher bonding temperatures and longer bonding times. The IMC thickness as a function of bonding time at 250 °C indicated that as the bonding time exceeded 2000 s, the (Co,Cu)Sn 3 growth rate increased significantly. Also, the (Co,Cu)Sn 3 phase started to grow rapidly at temperatures above 300 °C (the lowest bonding temperature at which detachment occurred with a bonding time of 1000 s). It can be concluded that the (Co,Cu)Sn 3 IMC grew rapidly once it nucleated. A rapid growth of (Co,Cu)Sn 3 has been reported to occur due to many diffusion paths available to elements in the (Co,Cu)Sn 3 crystal structure, which has low density [46]. As a result, Sn atoms diffused rapidly through both (Cu,Co) 6Sn 5 and (Co,Cu)Sn 3 to reach the Co substrate surface and grow further. The rapid growth of CoSn 3 has been discussed extensively [47–49].

Considering the bonding time and temperature of detached samples and the growth of CoSn 3, it can be concluded that the rapid growth of (Co,Cu)Sn 3 and total IMCs coincided with the detachment. As shown in Fig. 9a and b, the (Co,Cu)Sn 3 fraction was above 25% in all detached samples. In this work, the volumetric change due to (Co,Cu)Sn 3 formation is considered the same as that for CoSn 3 for formation from liquid Sn and solid Co, as the Cu content in CoSn 3 was not particularly noticeable. Therefore, the shrinkage of joints prepared at 250 °C for 3000 s caused by the formation of (Co,Cu)Sn 3 was calculated to be 13% using the following equation:

\[
\Delta V_{(\text{CoSn}_3)} = \frac{(M_{\text{CuSn}_3} + M_{\text{Cu}} + M_{\text{Sn}})}{(M_{\text{CoSn}_3} + 3M_{\text{Co}} + 3M_{\text{Sn}})} \times 100
\]

4.1.1. Phase equilibrium

Fig. 10 shows the calculated isothermal sections of the Cu–Sn–Co ternary system at 250 and 150 °C using the thermodynamic database created in this work. Based on the results, the maximum solubility of Co in the Cu 6Sn 5 phase is ~ 20 and 13 at% at 250 and 150 °C, respectively, which equilibrates to CoSn and Cu 3Sn. Cu 6Sn 5 containing 8–15 at% of Co at 250 °C and 8–11 at% of Co at 150 °C can be in equilibrium only with the CoSn 2 and Cu 3Sn phases. However, the CoSn 3 phase can be in equilibrium with Cu 6Sn 5 containing 7–8 at% of Co at 250 °C and 5–8 at% of Co at 150 °C. As discussed in Section 3.1, Cu 6Sn 5 with 12 at% of Co was adjacent to (Co,Cu)Sn 3 in detached samples. Therefore, the Co content in Cu 6Sn 5 exceeded the local phase equilibrium condition, whereas the Co contents in IMCs formed in samples successfully bonded and annealed for 1000 s were within the range of equilibrium. The dotted line I in Fig. 10 shows the observed reaction sequence for the successfully bonded samples. Two possible reaction sequences for fully IMC joints at a bonding temperature of 250 °C are illustrated in Fig. 10 with dotted lines II and III (either Cu 6Sn 5 with 12 at% of Co in equilibrium with CoSn 2 or Cu 6Sn 5 with 7–8 at% of Co in equilibrium with CoSn 3).
Fig. 9. (a) IMC thickness as a function of temperature for a bonding time of 1000 s (b) IMC fraction as a function of temperature for a bonding time of 1000 s (c) IMC thickness as a function of time at a bonding temperature of 250 °C. (d) IMC fraction as a function of time at a bonding temperature of 250 °C.

Fig. 10. Calculated isothermal section of Cu-Co-Sn at (a) 250 °C and (b) 150 °C.
...continuously on both sides in the IMC in samples. The Co content in Sample A changed continuously on both sides in the Co content in Cu6Sn5 at the IMC in a successfully bonded sample (Sample A) prepared at 250 °C for 1500 s and a detached sample prepared at 250 °C for 3000 s.

Fig. 11 shows the Co contents in the Cu6Sn5 phase from the Cu to the Co side in a successfully bonded sample (Sample A) prepared at 250 °C for 1500 s and a detached sample (Sample B) prepared at 250 °C for 3000 s, which are shown in Fig. 2d and f. An EDX line scan with 12 points over the reaction zone was performed on both samples. The Co content in Sample A changed continuously on both the Cu and Co sides. However, there was a significant difference between the two sides in the Co content in Cu6Sn5 at the IMC interface (2 and 8 at%, respectively). This significant discontinuous change in Co content is shown by a pink arrow in Fig. 11. Based on thermodynamic calculations, as shown in Fig. 10, (Cu,Co)6Sn5 with various amounts of Co can be in thermodynamic equilibrium only if the Co content changes continuously. Therefore, two interfaces showed changes in local phase equilibria: (Cu,Co)6Sn5/(Co,Cu)Sn3 and (Cu,Co)6Sn5 on the Co side and (Cu,Co)6Sn5 on the Co side. It can be concluded that the change in local thermodynamic equilibria is a plausible reason for the observed detachment. It should be emphasized that Co was adjacent to the (Cu,Co)6Sn5 in the sample successfully bonded at 250 °C for 1500 s and annealed at 150 °C for 1000 s. This is not possible from the stable local thermodynamic equilibria viewpoint. Based on the isothermal section, binary Co–Sn IMCs should be formed between Co and (Cu,Co)6Sn5, since Cu6Sn5 now seems to be in direct local metastable equilibrium with pure Co.

Finally, as shown in Fig. 4, (Cu,Co)6Sn5 with a high Co content (12 at%) formed on the Co side in detached samples had considerably finer grains than those with lower Co contents (2–8 at%). We can infer that both the high volumetric change owing to the rapid growth of (Co,Cu)3Sn on the Co side and the change in the local thermodynamic equilibrium led to detachment in the joint at the interface of fine- and coarse-grained (Cu,Co)6Sn5, where the local thermodynamic equilibrium was also altered. Therefore, to achieve reliable Cu–Sn SLID bonding using Co contact metallization, the thicknesses of Cu and Sn must be optimized to prevent significant Co dissolution and rapid CoSn3 growth in the interfacial layer. The thicknesses of Co consumed in the sample successfully bonded at 250 °C for 1500 s and the detached sample prepared at 250 °C for 3000 s were calculated to be 160 and 900 nm, respectively, using the following equation:

\[
X_{\text{Co}} = \frac{M_{\text{Co}}}{\rho_{\text{Co}}} \times \frac{\rho_{\text{Cu}6\text{Sn}5}}{M_{\text{Cu}6\text{Sn}5}} + \frac{6 \times \text{at.} \% \text{Co} \times \rho_{\text{CoSn}3} \times X_{\text{CuSn}5}}{M_{\text{CoSn}3}} + \frac{\text{at.} \% \text{Co} \times \rho_{\text{Sn}} \times X_{\text{Sn}}}{M_{\text{Sn}}}
\]

where \(M_{\text{Co}}, \rho_{\text{Co}}, \) and \(X_{x}\) are the molar weight, density, and thickness of component \(x\).

It should be noted that the density and molar mass of Cu6Sn5, CoSn3, and Sn were used without considering the impact of Co dissolved in Cu6Sn5 and Sn, and Cu dissolved in CoSn3 and Sn. Based on the estimation, \(X_{\text{consumed}}/X_{\text{Sn}}\) was 0.04 and 0.25 in the successfully bonded and detached samples at 250 °C, respectively.

5. Conclusion

This work investigated the microstructural evolution of a Cu substrate in contact with a Cu–Sn electroplated silicon chip to gain a deeper understanding of the potential use of Co for contact metallization for Cu–Sn SLID bonding. The results demonstrated that three phases were formed in the Cu–Sn –Co stack at bonding temperature ranges of 280–320 °C for 1000 s and 250 °C for 1500–3000 s: (Cu,Co)6Sn5, (Cu,Co)3Sn, and (Co,Co)Sn3. The bonding time and temperature determined which of these phases appeared in the interconnection microstructure. Co (2–12 at%) dissolved in Cu6Sn5 stabilized the high-temperature hexagonal crystal structure of Cu6Sn5 down to room temperature, which is consistent with the thermodynamic calculation results. The crystal orientations of Cu6Sn5 with low and high Co contents were similar. However, a higher Co content had a significantly greater effect on the refinement of the grains. The (Co,Cu)3Sn IMC required a higher bonding temperature-time average to form than (Cu,Co)6Sn5. Once (Co,Cu)3Sn formed, it grew rapidly. The content of Co dissolved in (Co,Cu)6Sn5 exceeded the condition of maximum Co content in Cu6Sn5 for thermodynamic equilibrium with (Co,Cu)3Sn. Furthermore, a local phase equilibrium was observed at the interface of (Co,Co)6Sn5 grown on the Cu and Co sides in detached samples. In higher temperature-time averages, a high (Co,Cu)3Sn growth rate and the formation of local nonequilibrium phases caused joints to detach.

Co can be deposited by physical vapor deposition, and it is CMOS/MEMS-compatible. Furthermore, this study shows that it is chemically compatible with the Cu–Sn system. Our experimental work and thermodynamic calculation results suggest that Co is excellent for contact metallization for Cu–Sn SLID bonding only if its thickness is limited to the critical value to ensure that its content in the Cu6Sn5 IMC remains low and rapid growth of CoSn3 is prevented. This means that the amount of dissolved Co must be controlled to achieve successful bonding in a Cu–Sn–Co SLID bonding system. According to the calculations in this study, Co and Sn must have an XCo-to-XSn thickness ratio of ≤ 0.04.

CRediT authorship contribution statement

M. Paulasto-Kröckel: Supervision, Conceptualization, Writing – review & editing. V. Vuorinen: Project administration, Conceptualization, Writing – review & editing. G. Ross: Writing – review & editing, Formal analysis. H. Dong: Thermodynamic...
modeling. Validation. F. Emadi: Formal analysis, Investigation, Writing – original draft, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


[34] C.H. Wang, S.E. Huang, K.T. Li, Inhibiting CoSn3 growth at the Sn/Co system by minor Zn addition, Intermetallics 56 (2015) 68–74.
