

Study of Low-Temperature Thermocompression Bonding in Ag-In Solder for Packaging Applications

RIKO I MADE,^{1,2,3} CHEE LIP GAN,^{1,2} LI LING YAN,³ AIBIN YU,³
SEUNG WOOK YOON,³ JOHN H. LAU,³ and CHENGKUO LEE^{3,4,5}

1.—School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, Singapore 639798. 2.—Advanced Materials for Micro- and Nano-Systems, Singapore-MIT Alliance, E4-04-10, 4 Engineering Drive 3, Singapore, Singapore 117576. 3.—Institute of Microelectronics, Agency for Science, Technology and Research (A*STAR), 11 Science Park Road, Singapore Science Park II, Singapore, Singapore 117685. 4.—Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore, Singapore 117576. 5.—e-mail: elelc@nus.edu.sg

Low-temperature solders have wide applications in integrated circuits and micro-electromechanical systems packaging. In this article, a study on Ag-In solder for chip-to-chip thermocompression bonding was carried out. The resulting joint consists of AgIn_2 and Ag_9In_4 phases, with the latter phase having a melting temperature higher than 400°C . Complete consumption of In solder into a Ag-rich intermetallic compound is achieved by applying a bond pressure of 1.4 MPa at 180°C for 40 min. We also observe that the bonding pressure effect enables a Ag-rich phase to be formed within a shorter bonding duration (10 min) at a higher pressure of 1.6 MPa. Finally, prolonged aging leads to the formation of the final phase of Ag_9In_4 in the bonded joints.

Key words: Low-temperature solder, indium, IC, MEMS, packaging

INTRODUCTION

Solid-liquid interdiffusion bonding consists of a multilayer of high-melting and low-melting materials to form a joint. Bonding is usually carried out at temperatures above the melting point of the low-melting material, during which the low-melting material is gradually consumed, resulting in a microjoint containing only intermetallic compounds (IMC). Through proper control of the multilayer film thickness and processing conditions, it is possible to form a joint free of the low-melting material.¹

In-based solders are attractive for low-temperature bonding due to their low melting temperatures. Furthermore, In reacts easily with a higher-melting counterpart such as Cu, Au or Ag, to form a wide variety of IMCs of high melting temperature. The concept of low-temperature bonding that achieves a high remelting temperature is attractive for applications such as micro-electromechanical systems

(MEMS) packaging, stacked-chips processes, and wafer-to-wafer bonding. Besides eliminating the undesirable phase transformation that occurs during high-temperature bonding, a low-temperature bonding process can reduce the process-induced residual stress of multilayer structures, while achieving a high post-package temperature resistance.

However, due to a high rate of interdiffusion within bonded couples formed between the noble metals and In, IMC formation can even occur at ambient temperature.²⁻⁴ As shown in Fig. 1, the solid solubility of In in Ag is much higher (approximately 20 at.% In in Ag) than that of Ag in In (<1 at.% Ag in In). At temperatures between the melting points of In (156.7°C) and Ag (961.9°C), solid Ag is dissolved in the molten In to form a eutectic compound and different IMCs. The melting point of these compounds increases with the Ag content, i.e., eutectic (144°C) $<$ AgIn_2 (166°C) $<$ γ (300°C) $<$ ζ (670°C) $<$ β (695°C).^{5,6}

In the mid 1990s, Roy and Sen⁷ assessed contact and composite resistances to monitor the evolution of interfacial reaction at different temperatures.

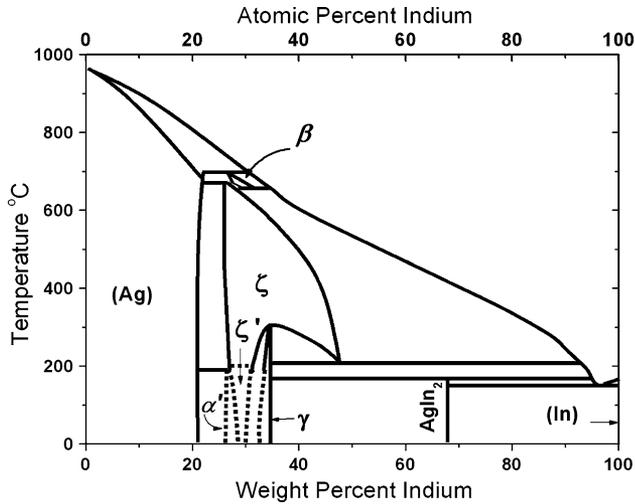


Fig. 1. Ag-In phase diagram. Redrawn from the ASM Handbook Online.

Through these measurements, it was reported that the formation of the AgIn_2 phase is a diffusion-controlled process with an activation energy of 0.43 eV. Lee et al. proposed a two-stage bonding-annealing process of the Ag-In thin layers, which consists of a short-duration exposure with temperatures slightly above 200°C , followed by a lengthy heat treatment in a hydrogen environment below 150°C . The high remelting temperature of the joint was produced by consuming all the In in the bonded couple to form an IMC phase of Ag_2In .^{3,8} Although the effects of bonding temperature and time have been investigated extensively,^{7,9} so far, the application of pressure during bonding has not been considered to be important to IMC phase formation. Bonding is usually carried out at low pressures.^{3,5,7-10} However, as the bonding temperature becomes lower, the morphology of the mating solder surface becomes more important. A microscopically rough surface is unavoidable and causes a reduction in the true contact area between the mating couple. Application of load in the form of higher pressure during bonding helps to flatten the surface, and thus may improve the true contact area.¹¹⁻¹³

The technique of simultaneous application of pressure and temperature during the bonding process is known as thermocompression bonding. Metallic bond formation takes place when the distance between the two substrates becomes so small that it is energetically favorable for surfaces to coalesce in order to eliminate the interfacial energy. The surfaces are brought closer together by the application of pressure. In this paper, we report on the formation of intermetallics from low-temperature thermocompression bonding of the Ag-In system. The focus of the study is on the effects of bonding parameters, especially the applied pressure, on the formation of IMCs at the bonding interface. The results shown could provide an alternative method

to produce high-temperature joints other than the conventional heat treatment method.

EXPERIMENT

The Ag-In multilayer structure for the low-temperature bonding study is shown in Fig. 2. Side A consists of a 50-nm-thick SiO_2 as the top layer, 25-nm-thick Cr (to improve the adhesion), 800-nm-thick In, and a 100-nm-thick Ag layer in the rear. The Ag layer was used as an oxidation-prevention layer, by reacting with In to form AgIn_2 during deposition.⁷ Similarly, side B consists of a 50-nm-thick SiO_2 , followed by 30-nm-thick Cr, 2.6- μm -thick Ag, and 30-nm-thick Au layers. The In layer on side A is thin enough such that it will be fully consumed to form IMCs by Ag on side B during thermocompression bonding. Upon uniform distribution of In at the bonding layer, the overall composition is approximately 17 at.% In. In other words, the average atomic ratio of a homogeneous phase depends on the layer structure thickness ratio, which is $\text{Ag}/\text{In} = 83/17$ in our solder system. From previous literature, it is suggested that the thickness of In on side A and Ag on side B determines the final phase composition of the bonding couple.⁸

The 50-nm-thick SiO_2 on both sides A and B was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 300°C on a 200-mm bare silicon wafer. The metal film stack was deposited on separate wafers for sides A and B. This was done in a single evaporation step without breaking the vacuum (10^{-5} Torr) to prevent In oxidation. Next, prepared wafers of both sides A and B were cut

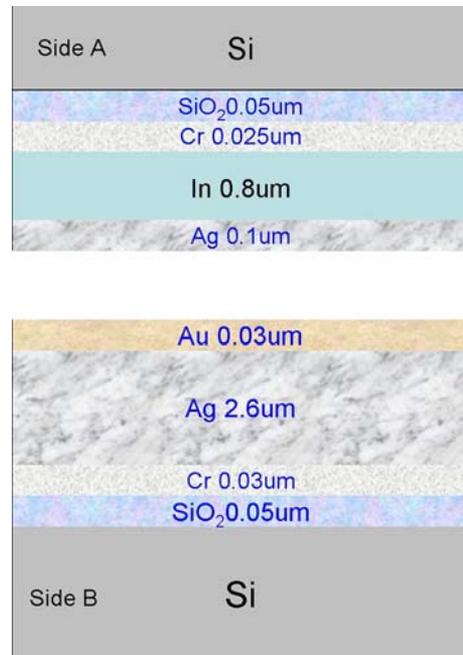


Fig. 2. Multilayer bonding couple design, In-rich on side A and Ag-rich on side B.

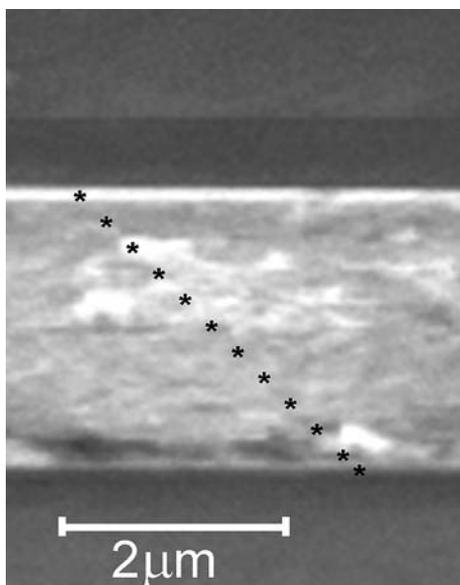


Fig. 3. EDX point array taken across bonding interfaces. The stars represent locations where EDX points were taken.

into squares of $5 \text{ mm} \times 5 \text{ mm}$. Thereafter, both sides were aligned and bonded at 180°C for varying times and pressures using a Suss FC150 flip-chip bonder. Temperature was only applied when the target pressure had been achieved. The thermo-compression cycle was completed by cooling down the bonder to room temperature while maintaining the applied pressure.

Several methods were used to characterize the bonded samples. Cross-section elemental composition was characterized by energy-dispersive x-ray spectroscopy (EDX). Samples were mounted on epoxy resin and subsequently polished. Arrays of EDX spectrum were taken from side B to side A to measure the element composition as a function of depth, as shown in Fig. 3. X-ray diffraction (XRD) was used to determine the exact phases that had formed under the various bonding conditions. Bonded samples were pulled apart by mechanical force to expose the bonded interface. XRD spectrum was then obtained using the Bruker-General Area Detector Diffraction System (GADDS). Several selected samples were also characterized by a differential scanning calorimeter (DSC) to determine the melting temperature of the phase that had formed at different bonding conditions.

RESULTS

It has been reported that Ag diffuses rapidly into In via an interstitial mechanism, whereas In diffuses into Ag through grain boundaries.^{9,10} Earlier studies had also confirmed that the In film at side A led to the formation of a AgIn_2 layer on the surface upon deposition.^{4,9}

Figure 4 shows the EDX scans of cross-sectioned samples bonded at 1.4 MPa and 180°C for different

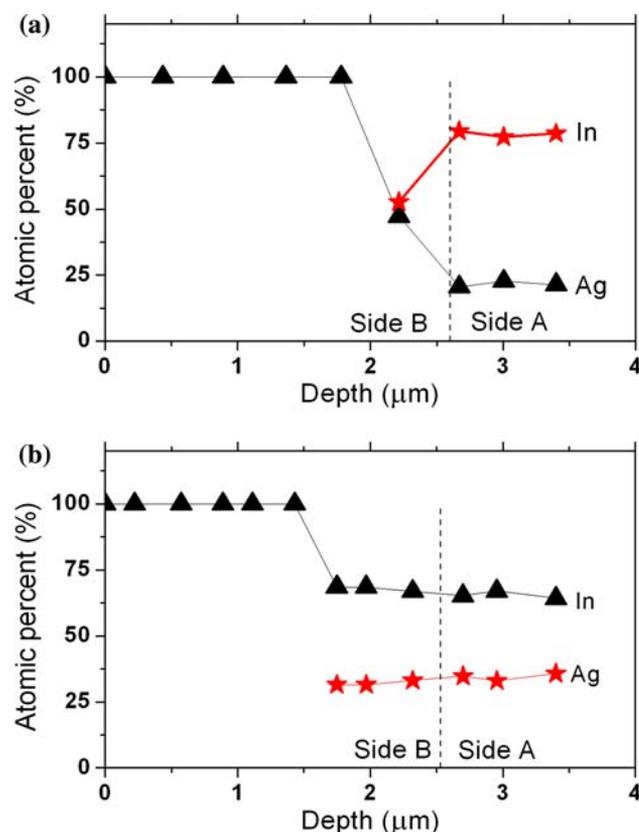


Fig. 4. EDX cross-section scans from couples bonded at 1.4 MPa and 180°C and for two different bonding times. Zero reference was taken from the Ag-Cr interface, where for (a) the 10-min (short) bonding time, Ag had diffused further into side A compared with In into side B, and (b) 40-min (long) bonding time, the average composition of In in the Ag-In IMC saturates at around 34 at.% In, close to the composition of Ag_2In or Ag_9In_4 . Note also a pure-Ag region in side B for both cases.

durations (10 min and 40 min). The dashed line on each of the plots indicates the original bonding interface where sides A and B initially met. The cross sections consist of pure Ag, Ag-rich, and In-rich regions. It is also observed that Ag diffused further into the In region for the longer bonding time. The XRD analysis supports our observations that the bonding couple is dominated by the AgIn_2 phase for short bonding duration, and Ag_9In_4 for long bonding time on side A. By DSC characterization, the Ag_9In_4 phase has a remelting temperature of more than 400°C .⁴

To study the effect of bonding pressure on IMC formation, several samples were bonded at 180°C for 10 min with a bond pressure varying from 1.0 MPa to 1.6 MPa. Cross-sectional EDX analysis of the samples are shown in Fig. 5. It is observed that the depth of In diffusing from side A (In-rich side) to side B (Ag-rich side) becomes smaller as the applied bonding pressure increases. On the other hand, Ag diffusion from side B to A seemed to be independent of bond pressure. Although no 100% In region was found based on the EDX analysis, XRD

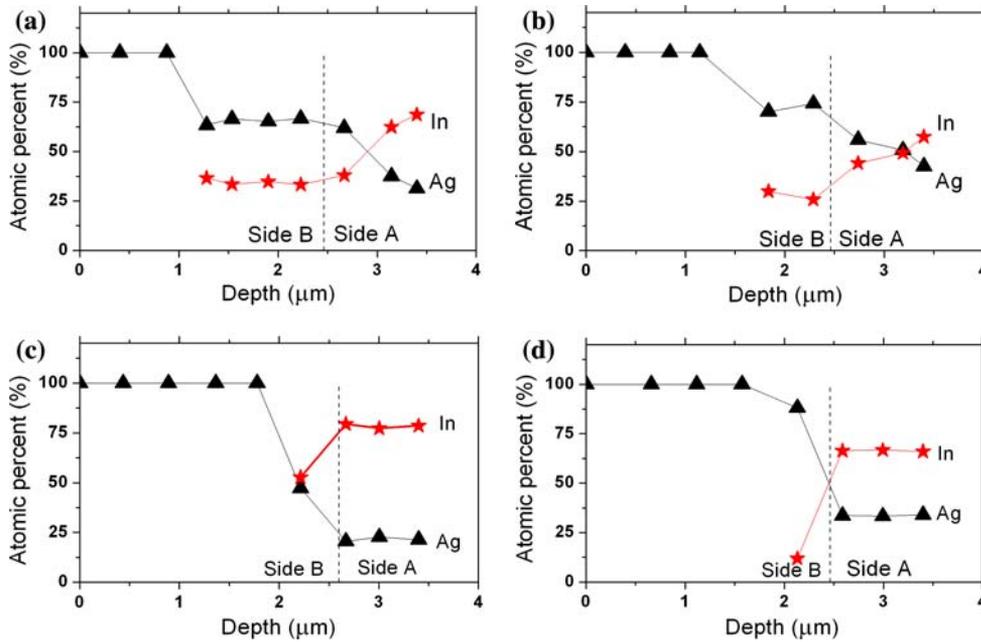


Fig. 5. EDX cross-section scans from bonded couples at 180°C for 10 min at different bonding pressures: (a) 1.0 MPa, (b) 1.2 MPa, (c) 1.4 MPa, and (d) 1.6 MPa. Zero reference was taken from the Ag-Cr interface.

detected an In phase on side A at 1.0 MPa and 1.2 MPa bond pressure besides AgIn_2 (Fig. 6). We postulate that the In-rich regions shown in Fig. 5a and b could be a mixture of unreacted In and AgIn_2 phases. On the other hand, the phase is dominated by Ag_9In_4 for a bonding pressure of 1.6 MPa.

Figure 7a shows the EDX result of a sample cross section bonded at 1.4 MPa for 10 min at 180°C with an additional aging at 70°C for 17 h. It is observed that the cross section consists of pure-Ag and Ag-rich regions. Phase identification for different aging times was done in an earlier study.⁴ With no aging, side A of the bonding couple is mostly dominated by AgIn_2 , whereas samples aged for 17 h at 70°C contain only the IMC phase of Ag_9In_4 . With further aging up to 30 h, the AgIn_2 phase was detected again.

Figure 7b shows the EDX result of another sample that was kept at room temperature for 6 months. It is also observed that the cross section consists of pure-Ag and Ag-rich regions, similar to those aged at 70°C for 17 h. Figure 8 shows XRD data of a sample that underwent an additional 6 months of room-temperature storage, exhibiting coexistence of the AgIn_2 and Ag_9In_4 phases.

DISCUSSION

From the presented results, we deduce that there are several relationships between IMC formation and the bonding parameters. During the bonding process at 180°C, the In film melts while Ag remains as a solid and dissolves into the molten In. Since the solubility limit of Ag in In is low (<1 at.% Ag in In),

further supply of Ag is expected to drive the formation of Ag-In IMCs.⁶

Effect of Bonding Time

The duration of bonding determines the IMC that will form through the supersaturation of Ag in molten In. At temperatures above the In melting point, the melt erodes the solid Ag. Given sufficient bonding time, Ag dissolves in the molten In and reaches the solubility limit. Further supply of Ag would drive the formation of the IMC preferred at the particular temperature. From the phase diagram, a Ag-rich IMC is the preferred phase at a bonding temperature of 180°C. Thus, the majority phase formed at the long bonding time (40 min) is Ag_9In_4 . This is in agreement with an earlier published result in which a Ag-rich preferred phase was formed at a higher annealing temperature over a longer duration.^{4,10}

On the other hand, for short bonding duration, some regions in the bonded couple may not exceed the Ag solubility limit at the particular bonding temperature. Thus no IMC formation can be initiated. This is especially true for regions that are relatively far from the Ag reservoir with insufficient time for In diffusion and Ag dissolution. However, as the temperature is lowered (during cooling), the Ag become less soluble in In, and the extra Ag solute would eventually lead to the formation of an IMC. From Fig. 1, an In-rich AgIn_2 phase would tend to form first for a liquid transition temperature lower than 166°C. AgIn_2 IMC was also detected for samples bonded for short bonding time (10 min), which may have formed during cooling.

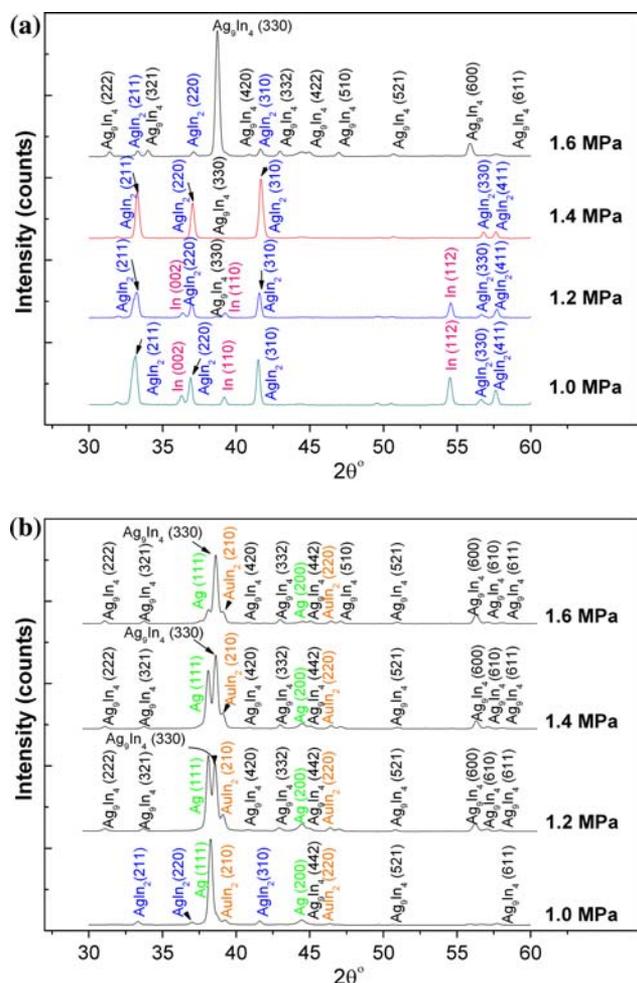


Fig. 6. Effect of bonding pressure on IMC formation for bonding at 180°C for 10 min. (a) On side A, Ag_9In_4 is the dominant phase as the bonding pressure increases. (b) On side B, consistent with side A, Ag_9In_4 is the dominant phase as the bonding pressure increases.

Effect of Bonding Pressure

There are three factors that could drive Ag-rich IMC phase formation at high pressure: (1) a reduction in In supply as the pressure increases due to changes in the melting temperature of pure In, (2) a decrease in the AgIn_2 to Ag_9In_4 transition temperature as pressure increases,¹⁴ and (3) an increase in force with higher pressure that flattens more asperities on a rough surface, thus increasing contact between the two mating surfaces.¹²

The applied pressure was found to change the melting temperature of the metal stack during the bonding process. In turn, changes in the pure melting temperature of In would affect the quantity of melt, thus affecting the reaction kinetics. The pressure-dependent melting temperature of materials is defined thermodynamically by the Clapeyron equation,¹⁴

$$T \propto T_1 e^{\left(\frac{\Delta V}{\Delta H} P\right)}, \quad (1)$$

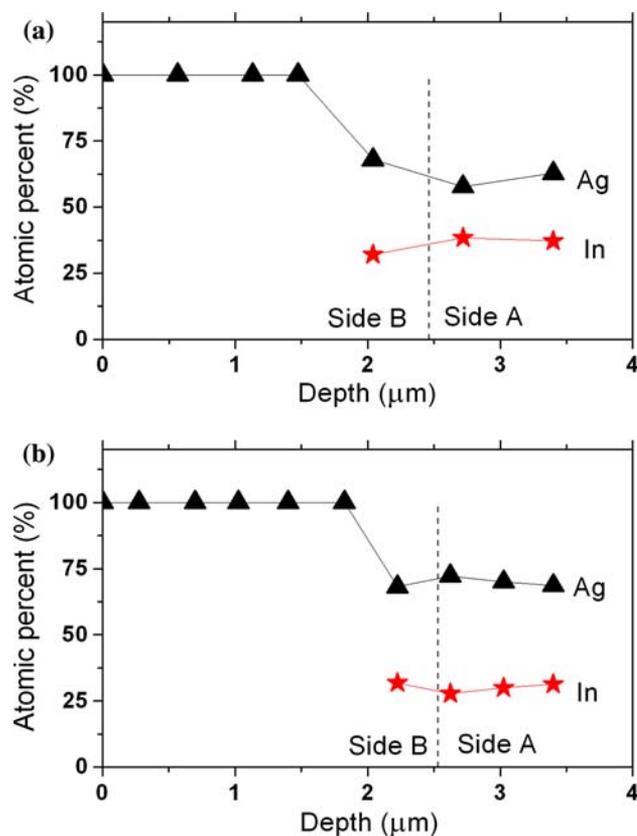


Fig. 7. (a) Results of EDX scans of samples aged at 70°C for 17 h, showing the preferred Ag-rich phase. This sample was bonded at 1.4 MPa at 180°C for 10 min. (b) Results of EDX scans of samples aged at room temperature for 6 months compared with just-bonded sample; samples bonded at 1.4 MPa at 180°C for 10 min.

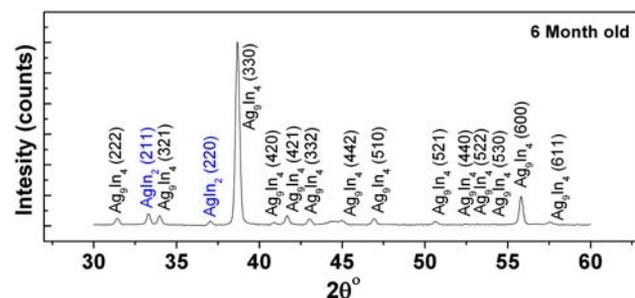


Fig. 8. Results of an XRD scan of samples aged at room temperature for 6 months; samples bonded at 1.4 MPa at 180°C for 10 min.

where T is the phase-change temperature, P is the pressure, T_1 is the phase-transition temperature at standard pressure (1 atm), ΔH is the change in enthalpy of fusion in the solid–liquid transition, and ΔV is the change in system volume. ΔH is usually considered to be weakly dependent on pressure. ΔH and ΔV are both positive for solid-to-liquid transition. These positive parameters in the exponential factor of Eq. 1 translates to an increase in the transition temperature as the pressure increases. With an increase in the In melting temperature,

there would be less supply of molten In, leading to a reduction of the solid-liquid reaction and In diffusion. Furthermore, as the supply of Ag is virtually unlimited, liquid In quickly becomes Ag-saturated, which may initiate Ag-rich IMC nucleation (Ag_9In_4).

Thus, with increasing bond pressure and decreasing melting temperature of pure In, only regions that are near the In-Ag interface are able to form IMCs. If the In film is too thick, regions that are further from the bonding interface may only form an In-rich solid solution or even pure In, and a Ag-rich phase would form near the bonding interface. As shown in Fig. 5d, EDX confirms that high concentrations of In phase were detected at locations further from the bonding interface, even though the XRD characterization (Fig. 6) determines that a Ag-rich phase tends to dominate at high bonding pressure.

The second factor is the change in the AgIn_2 to Ag_9In_4 transition temperature. In the Ag-In system bonding, AgIn_2 has a lower mass density (8.23 g/cm^3) than Ag_9In_4 (9.90 g/cm^3), which translates into a negative ΔV . From Eq. 1, the phase-transition temperature for AgIn_2 to Ag_9In_4 will decrease as the bonding pressure increases.

From the perspective of contact mechanics, the application of pressure will flatten the asperities on rough surfaces, and lead to an increase in the contact area and diffusion paths between the two bonded couples. Both sides of the bonding couple are expected to be microscopically rough. At low bonding pressure, less force was applied to flatten the asperities, which resulted in a low contact area. Conversely, at higher bonding pressure, the contact area would be higher and improve the diffusion paths for In and Ag interdiffusion.

Effect of Aging

Post-treatment aging allows a system to obtain its most stable phase formation. Unlike the bonding process, all reactions during aging are controlled by solid-state diffusion. During the initial bonding, molten In in contact with the Au layer on side B forms a highly stable AuIn_2 phase which is unlikely to dissociate or further react with In or Ag, up to 300°C . However, this stability could also reduce the In and Ag interdiffusion from side A to B and vice versa, respectively. In diffusion is further inhibited due to the larger In atomic size as compared with Ag. Thus, with a larger flux of Ag from side B into side A, all the In will be converted into the Ag-rich phase (Ag_9In_4) first.

According to Chuang et al., Ag_9In_4 is energetically unstable in long-term aging at temperatures lower than 75°C . Thus, Ag_9In_4 tends to evolve back into AgIn_2 to maintain a lower energy state with a sufficient supply of In.¹⁰ As the supply of In in our specimens is limited, only a portion of the Ag_9In_4 phase is converted into AgIn_2 . Hence as a compromise, the two phases of Ag_9In_4 and AgIn_2

coexist and remain stable for a long duration, as demonstrated in our 6-month study at room temperature (Fig. 8).

CONCLUSION

A low-temperature soldering process can avoid the concern of residual stresses that are typically introduced by thermal expansion mismatch during the cooling step in a high-temperature soldering process. Since the resulting joints need to withstand higher post-bonding temperature processing, a solder system that can form high-temperature IMCs at the joint at a low bonding temperature is required. We have studied pressure, temperature, and bonding time parameters and their effects on IMC formation in the Ag-In solder system. We observed that the bonding duration determines the supply of Ag in the molten state. For a long bonding time, Ag reaches supersaturation in the In melt and drives the formation of a Ag-rich IMC phase. In-rich phase forms during cooling for short bonding durations. The results show that the bonding condition of 180°C at 1.4 MPa for 40 min is sufficient to consume all the In so as to give a final major phase of Ag_9In_4 . A higher bonding pressure under solid-liquid reaction was also found to enhance the formation of Ag_9In_4 . Three factors that could drive a Ag-rich IMC phase formation at high pressure are proposed: (1) a reduction in In supply as pressure increases due to changes in the melting temperature of pure In, (2) a decrease in the AgIn_2 to Ag_9In_4 transition temperature as pressure increases, and (3) an additional applied force to flatten the asperities on a rough surface, thus creating more contact area between the two mating surfaces. This also implies that Ag_9In_4 can be obtained within a shorter duration at a higher pressure as well. We have proven that bonding pressure is an important factor that thus needs to be considered and optimized for low-temperature solder bonding.

In conclusion, complete consumption of low-melting-temperature In to form a high-melting-temperature IMC phase, in this case Ag_9In_4 , can be achieved by two main approaches. Firstly, bonding at 180°C under a pressure higher than 1.4 MPa for sufficient time can lead to Ag_9In_4 being the dominant phase. Secondly, for a Ag-to-In film thickness ratio of 83/17, a joint that consists of a mixture of AgIn_2 and Ag_9In_4 phases can be converted into a joint with Ag_9In_4 as the dominant phase after long-term room-temperature storage and/or a few days of low-temperature aging. These findings may lead to the formation of bonded joints with high-temperature-resistant IMCs at relatively low bonding process temperature for applications in IC and MEMS packaging.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the School of Materials Science and Engineering at Nanyang

Technological University (NTU), Singapore, for providing a scholarship to Riko I Made. The authors would also like to thank the Institute of Materials Research Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), Singapore, for assistance with the Bruker-General Area Detector Diffraction System (GADDS). Chengkuo Lee, PI of IME Core Project 06-420004, would like to thank the Institute of Microelectronics, Agency for Science, Technology and Research (A*STAR), Singapore, for providing research funding for this research.

REFERENCES

1. F. Bartels, J. Morris, G. Dalke, and W. Gust, *J. Electron. Mater.* 23, 787 (1994). doi:[10.1007/BF02651374](https://doi.org/10.1007/BF02651374).
2. F.S. Shieu, C.F. Chen, J.G. Sheen, and Z.C. Chang, *Thin Solid Films* 346, 125 (1999). doi:[10.1016/S0040-6090\(98\)01737-4](https://doi.org/10.1016/S0040-6090(98)01737-4).
3. R.W. Chuang and C.C. Lee, *Thin Solid Films* 414, 175 (2002). doi:[10.1016/S0040-6090\(02\)00424-8](https://doi.org/10.1016/S0040-6090(02)00424-8).
4. R.I. Made, C.L. Gan, C. Lee, L.L. Yan, Ai. Yu, S.W. Yoon, and J.H. Lau, *Proc. SPIE* 6884, 68810H (2008). doi:[10.1117/12.762046](https://doi.org/10.1117/12.762046).
5. J.-C. Lin, L.-W. Huang, G.-Y. Jang, and S.-L. Lee, *Thin Solid Films* 410, 212 (2002). doi:[10.1016/S0040-6090\(02\)00240-7](https://doi.org/10.1016/S0040-6090(02)00240-7).
6. T.B. Massalski, H. Okamoto, P.R. Subramanian, and L. Kacprzak, *ASM Handbook*, Vol. 3 (Material Park, OH: ASM International, 1992).
7. R. Roy and S.K. Sen, *Thin Solid Films* 197, 303 (1991). doi:[10.1016/0040-6090\(91\)90241-O](https://doi.org/10.1016/0040-6090(91)90241-O).
8. R.W. Chuang and C.C. Lee, *IEEE Trans. Compon. Packag. Technol.* 25, 453 (2002). doi:[10.1109/TCAPT.2002.801113](https://doi.org/10.1109/TCAPT.2002.801113).
9. V. Simic and Z. Marinkovic, *Thin Solid Films* 61, 149 (1979). doi:[10.1016/0040-6090\(79\)90457-7](https://doi.org/10.1016/0040-6090(79)90457-7).
10. T.H. Chuang, Y.T. Huang, and L.C. Tsau, *J. Electron. Mater.* 30, (2001). doi:[10.1098/rspa.1966.0242](https://doi.org/10.1098/rspa.1966.0242).
11. J.A. Greenwood and J.B.P. Williamson, *Proc. R. Soc. Lond. A* 295, 300 (1966). doi:[10.1098/rspa.1966.0242](https://doi.org/10.1098/rspa.1966.0242).
12. H.L. Leong, C.L. Gan, C.V. Thompson, K.L. Pey, and H.Y. Li, *J. Appl. Phys.* 102, 103510 (2007). doi:[10.1063/1.2811724](https://doi.org/10.1063/1.2811724).
13. H. Hertz and J. Regine Angew, Translated and reprinted in English in *Hertz's Miscellaneous Paper* (London: Macmillan & Co., 1986).
14. D.A. Porter and K.E. Easterling, *Phase Transformations in Metals and Alloys* (London: Chapman & Hall, 1992).