

# Interfacial Reactions between Liquid Indium and Au-Deposited Substrates

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The morphology and growth kinetics of intermetallic compounds formed during the soldering reactions of liquid indium on Au-deposited substrates in the temperature range of 225°C and 350°C have been investigated. The results show that two types of AuIn<sub>2</sub> intermetallic compounds make their appearance: the continuous-wavy-crystalline type, and the floating-island type. The growth of this intermetallic compound follows the parabolic law, which indicates that the growth is diffusion-controlled. The activation energy of the reaction calculated from the Arrhenius plot of growth reaction constants is 39.42 kJ/mol. Also, the wettability of liquid indium on the surface of the gold-deposited substrate is determined from contact angle measurements. Finally, a mechanism for the interpretation of the wetting behavior of the said Au/In system is proposed, which can be ascertained by SEM observations.

**Key words:** Gold, indium, soldering, intermetallic compound, activation energy, wettability

## INTRODUCTION

Soldering has been widely employed in electronic packaging processes where surface mounting technology (SMT), flip chip bonding (FC) and ball grid array (BGA) are concerned. There are many solder alloys used for commercial purposes, among which the PbSn alloys are the most popular on account of their bounteous merits such as wettability, fatigue resistance, corrosion resistance, and, competitive pricing. However, adaptation to lead-free solders, out of environmental concerns, has become a top priority in the electronics industry.

Among a slew of lead-free solders developed recently,<sup>1-3</sup> indium-based alloys have been favored in bonding devices that demand low soldering temperatures.<sup>4</sup> Shimizu et al.<sup>5</sup> have indicated that indium-based solders possess excellent mechanical properties, as they display a more enduring fatigue life than PbSn solders in the flip-chip process, and are suitable for the role of high reliability interconnections. Indium has also been added to a number of other lead-free solders in order to increase wettability and lower the melting points.

On the other hand, gold-studs or bumps have also been employed for flip chip attachment. In other flip chip techniques, gold is an important element used as

the oxidation protective layer in under bump metallurgy (UBM) and top surface metallurgy (TSM).<sup>6</sup> In addition, the microsoldering of the Au/In/Au layer for electronic contacts has been demonstrated by Mil'shtein et al. as to exhibit good strength,<sup>7</sup> and the thermo-compression bonding of indium with gold bumps has also been adopted for LCD panels.<sup>8</sup> In another microjoining technique known as solid-liquid interdiffusion bonding (SLID, based on the formation of a thin intermetallic compound layer through reactions between metallic layers with respectively higher and lower melting points), the Au/In system has also been successfully employed.<sup>9</sup> Although the Au/In or Au/PbIn interfacial reactions have been studied by several researchers, their efforts have targeted primarily on solid/solid reactions,<sup>10-17</sup> whereas information regarding liquid/solid soldering reactions is limited thus far.<sup>18</sup> In respect of solid-solid-state reactions, Powell and Braun's investigations<sup>10</sup> on the bulk diffusion of Au/In at temperatures below the melting point of indium showed that four intermetallic compounds AuIn<sub>2</sub>, AuIn, Au<sub>7</sub>In<sub>3</sub>, and Au<sub>4</sub>In were formed, with AuIn<sub>2</sub> as the major layer on the reaction zone. In their study of thin film diffusion coupling of Au/In, Simic et al.<sup>11</sup> showed that the Au and In interdiffusion took place quickly at room temperature, which resulted in the appearance of AuIn<sub>2</sub>, AuIn, Au<sub>7</sub>In<sub>3</sub>, and Au<sub>4</sub>In intermetallic compounds. They also pointed out that formation of the above intermetallic com-

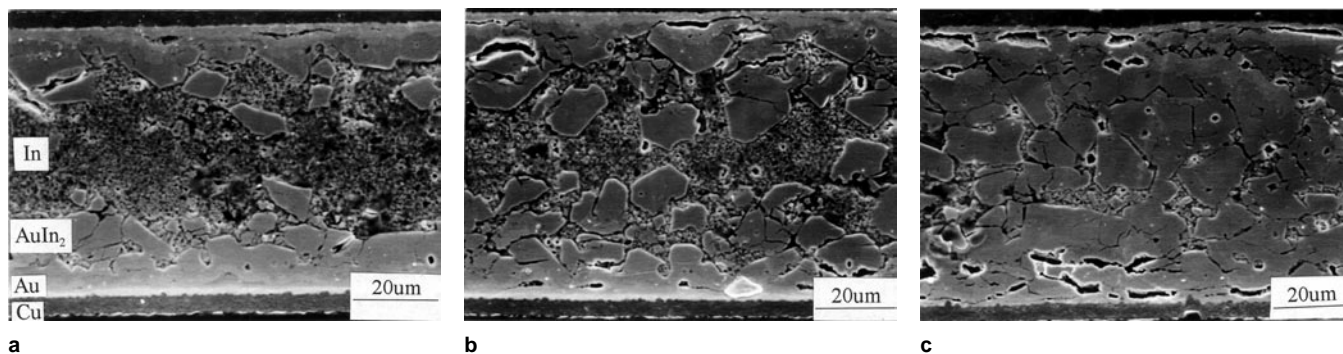


Fig. 1. Morphology of intermetallic compounds formed during interfacial reaction between In and Au at 300°C for (a) 5 min, (b) 15 min, (c) 20 min.

**Table I. Chemical Composition of the Intermetallic Compounds Formed in the Interfacial Reaction**

Temp.	I.P. Phase	I.M. Position	Au (at.%)	In (at.%)	Cu (at.%)
225°C	AuIn <sub>2</sub> (Cu)	Continuous Layer	30.0	69.6	0.4
25 min		Floating Island	30.5	69.2	03.3
250°C	AuIn <sub>2</sub> (Cu)	Continuous Layer	32.4	65.6	2.0
25 min		Floating Island	31.6	66.8	1.6
300°C	AuIn <sub>2</sub> (Cu)	Continuous Layer	30.8	66.2	3.0
25 min		Floating Island	30.6	66.8	2.6
325°C	AuIn <sub>2</sub> (Cu)	Continuous Layer	29.3	64.7	6
25 min		Floating Island	30.7	66.5	2.8

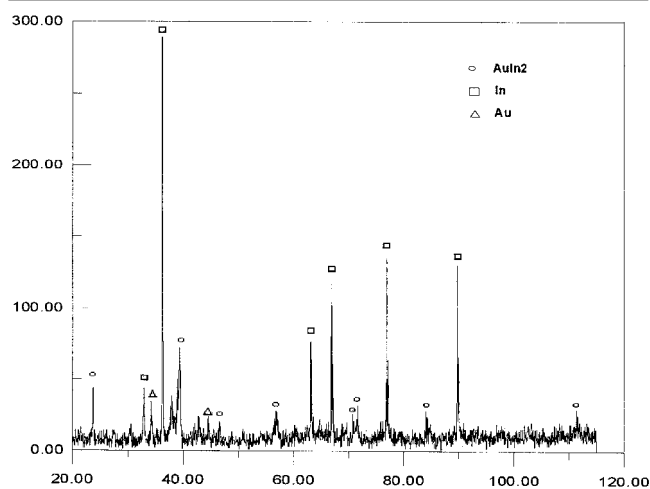


Fig. 2. Typical x-ray diffraction pattern of the In/Au interfacial reaction products formed at 350°C for 20 min.

pounds relied much on the Au/In film thickness ratio and diffusion time, and AuIn<sub>2</sub> was always the first phase formed. The study of Au/In thin film reactions by Bjøntegaard et al.<sup>12</sup> and Hasumi<sup>13</sup> showed that only the AuIn<sub>2</sub> compound was formed by In atoms diffusing through the preformed AuIn<sub>2</sub> to react with Au atoms, and, from a kinetic point of view, the well-known parabolic law was obeyed. In contrast, Millares et al.<sup>14</sup> studied the AuIn<sub>2</sub> growth from bulk diffusion couples, and demonstrated a linear kinetics for AuIn<sub>2</sub> layer growth in short-time reaction, which implied that the reaction was interface controlled. Yost et al.<sup>15, 16</sup> have studied the aging of Au/PbIn solder joints. They found that a thin single-phase layer of Au<sub>3</sub>In<sub>4</sub> and a thick dual-phase layer of AuIn<sub>2</sub> equiaxed grains impeded in

Pb were formed in the aging process. The total reaction layer thickness vs. time could be well defined in a linear relationship, which implied that the growth of intermetallic compounds was interface controlled and the activation energy was 0.61 eV. In the solid state reaction of Au/In48Sn, Shohji et al.<sup>17</sup> found a double layer of AuIn<sub>2</sub>/Sn-rich  $\gamma$ -phase formed on the interface between the Au substrate and the In48Sn solder. The AuIn<sub>2</sub> layer grew toward the In48Sn solder, showing that the diffusion rate of Au atoms through the AuIn<sub>2</sub> layer was much greater than that of In atoms. The growth of the AuIn<sub>2</sub> layer followed the parabolic law, and the activation energy, which corresponded to the activation energy for the diffusion of Au atoms in AuIn<sub>2</sub>, was 42.8 kJ/mol.

In contrast to plentiful investigations on Au/In solid state reactions, those on liquid/solid reaction are seldom. Jacobson<sup>18</sup> indicated that Au formed a continuous layer-type interfacial compound of AuIn<sub>2</sub> with In when heated above the melting point of In. Once formed, this AuIn<sub>2</sub> layer would act as an effective dissolution barrier for Au to dissolve into the In solder. However, no detailed kinetic data have been available thenceforth.

In this present study, the morphology of the interfacial compounds and kinetics of the soldering reaction of liquid In and solid Au deposited Al<sub>2</sub>O<sub>3</sub> substrates have been investigated. In addition, since the knowledge of wetting behavior of the In solder on Au substrates is essential to their applications, the wettability of liquid indium on gold substrates is also evaluated.

## EXPERIMENTAL

The Au layer with a thickness of 6  $\mu$ m was deposited on an Al<sub>2</sub>O<sub>3</sub> substrate by sputtering. For the improve-

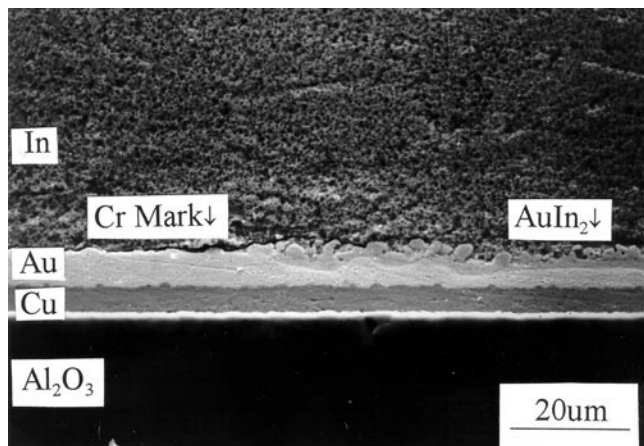


Fig. 3. Migration of  $In_0/Au_{(s)}$  interface toward the Au substrate after soldering reaction at 250°C for 10 min. (The original interface was marked with a Cr thin film.)

ment of adhesion between Au and  $Al_2O_3$ , a Cu interlayer with a thickness of 4  $\mu m$  was employed. Specimens of a size of 8 mm  $\times$  8 mm were cut from the substrates and then ultrasonically degreased in acetone. The indium solder was rolled from an In ingot with 99.99% purity into a 0.2 mm-thick foil. The foil was cut to the same size as the Au-deposited substrate.

For testing the soldering reaction, an In foil was inserted between two Au-deposited substrates. The sandwiched sample was heated in an IR furnace under a vacuum of  $10^{-3}$  torr. Soldering was conducted between 225°C and 350°C from 5 to 30 min. The sample was then cooled down to room temperature in 2 min by water cycling as pertained to the heating stage.

The soldered specimens were cut along the cross-section, ground with SiC paper, polished with 1 and 0.3  $\mu m$   $Al_2O_3$  powders and deposited with carbon in the vacuum evaporator to avoid the charging phenomenon of the  $Al_2O_3$  substrate in SEM or EPMA. Morphology observations were mostly conducted through applying a scanning electron microscope (SEM). Intermetallic compounds were identified with electron probe micro analyzer (EPMA) and x-ray diffractometer (XRD). To prepare for the XRD analy-

sis, the chosen specimens were selectively etched with a solution of 10 ml HF, 10 ml  $H_2O_2$  and 40 ml  $H_2O$ , so that the In solder would dissolve and the intermetallic compounds would remain. As the formation mechanism of intermetallic compounds in the soldering reaction ought to be clarified, certain Au-deposited  $Al_2O_3$  substrates were sectionally marked by sputtering-deposition of a Cr thin film. From the phase diagram, it could be observed that Cr would not react with In, and the deposition of a Cr thin film on an Au substrate worked as a diffusion barrier at the  $In_0/Au_{(s)}$  interface. Thus, the original  $In_0/Au_{(s)}$  interface could be identified.

The wettability of liquid indium on Au-deposited substrates was evaluated by measuring the contact angles of the indium sessile drop on the Au-deposited  $Al_2O_3$  substrate at the temperatures of the soldering reaction. The measurement was carried out by placing an indium cylinder of 2 mm in diameter and 2 mm in height on an Au-deposited  $Al_2O_3$  substrate in an IR furnace under a  $10^{-3}$  torr vacuum. Prior to measuring, the indium cylinders were dipped with a mildly activated rosin flux. During the heating process, the variation of the contact angles with time was recorded by an in-situ video system.

## RESULTS AND DISCUSSION

The morphology of the Au/In/Au joint after soldering reactions at 300°C for various lengths of time was shown in Fig. 1. Two main types of intermetallic compounds turned out during the soldering process: the continuous wavy type on the Au/In interface and the floating-island type in the interior matrix of the indium solder. Both types of intermetallic compounds grew with the increase of reaction time and soldering temperature. The compositions of both intermetallic compounds were analyzed by EPMA and shown in Table I. These results were averaged from the data taken from at least five spots of the intermetallic compounds. It revealed that both types of intermetallic compounds possessed a similar composition of the  $AuIn_2$  phase. The x-ray diffraction pattern shown in Fig. 2 also confirmed that the intermetallic compounds

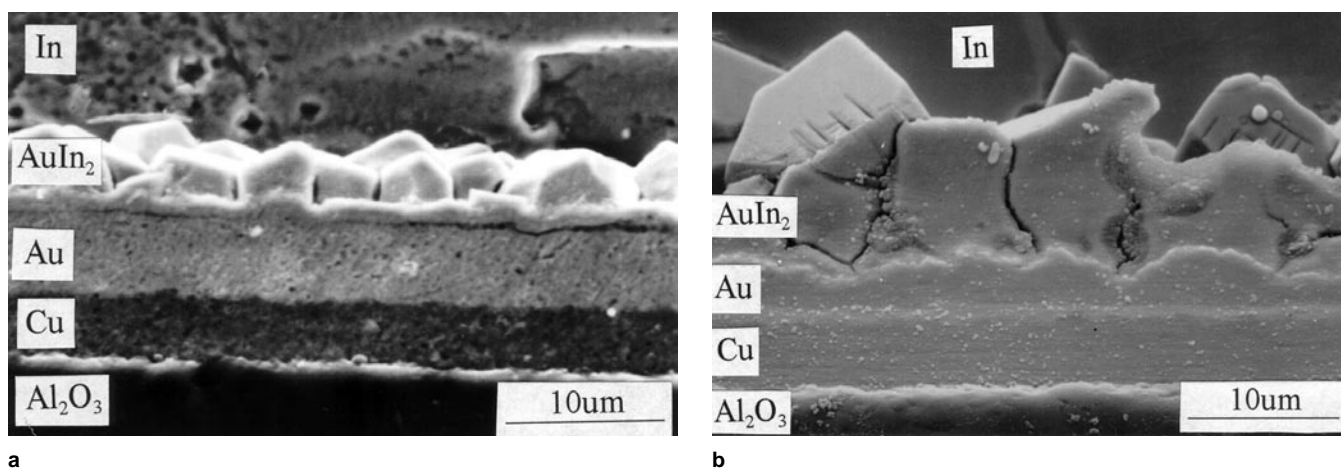


Fig. 4. Appearance of granular intermetallic compounds formed during In/Au interfacial reactions. (a) 300°C, 10 min; (b) 300°C, 20 min.

formed in the soldering reaction was of the  $\text{AuIn}_2$  phase.

In a study on the solid-liquid reaction of Cu/Sn, Ni/Bi and Cu/In systems, Kao<sup>19</sup> showed that the rapid dissolution of substrate atoms into the liquid solder would form an irregular structure of interfacial intermetallic compounds. On the other hand, the reaction between a substrate and a solder saturated with the substrate metal, as the dissolution would be inhibited in this case, would produce a more regular intermediate layer structure. Consistent with Kao's findings, the irregular shape of  $\text{AuIn}_2$  compounds formed at the Au/In interface in the current study should also be attributed to the rapid dissolution of Au into the In solder. Such a mechanism could be reaffirmed by referencing the study of Tu et al.,<sup>20</sup> in which they indicated that the fast dissolution of Au in the PbSn alloy, pure Sn, Sn4Ag and Sn20In2.8Ag alloys would incur a sunken curvature in the reaction interface, as well as intermetallic compounds precipitating in the solder matrix while cooling. In this present study, through sputtering a Cr thin film on the partial surface of the Au substrate to function as a diffusion marker for the  $\text{Au}_{(s)}/\text{In}_{(l)}$  soldering reaction, the  $\text{Au}_{(s)}/\text{In}_{(l)}$  interface was found to migrate toward the Au substrate and form a sunken curvature in the area adjacent to the Cr marker (Fig. 3). In addition, the appearance of floating-island-type intermetallic compounds in the In solder matrix (as shown in Fig. 1) also confirmed the results of Tu et al.<sup>20</sup>

Through selectively etching the remaining indium solder on the polished surface of the specimens, it was found (as shown in Fig. 4) that the continuous wavy type of intermetallic compounds was a layer of equiaxed grains grown from the Au/In interface into the indium solder matrix. A similar appearance of granular intermetallic compounds on the interface has also been observed by Yost et al. in their study of the interfacial reaction of the Au/PbIn system.<sup>15</sup> It was also found in the current study that during the reaction, the granular intermetallic compounds grew in size while decreasing in number (see Fig. 4a and b). This implied that a ripening effect occurred accompanying the growth of intermetallic compounds.

Since Au manifested no solubility in solid In, the floating-island type of intermetallic compounds in the indium solder should result from Au atoms dissolving in liquid indium during the soldering reaction, and then starting to precipitate after cooling down from the soldering temperature. However, as the reaction time was stepped up, some of the intermetallic compounds in the continuous wavy layer would split away from the interface and float into the indium solder to form more island-type intermetallic compounds in the solder matrix.

As Table I delineated, the concentration of the dissolved Cu in the  $\text{AuIn}_2$  phase would rise with the increase of soldering temperature and time. The reason for the Cu impurity existing in the  $\text{AuIn}_2$  phase could be traced to the outward diffusion of the Cu adhesive layer between Au and the  $\text{Al}_2\text{O}_3$  substrate. During the soldering reaction between liquid In and

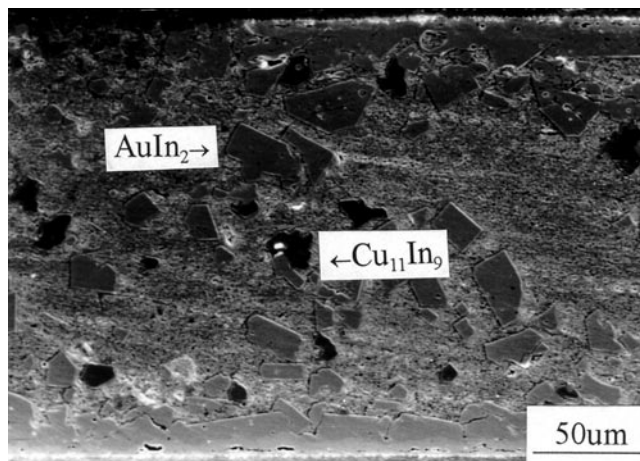


Fig. 5. Simultaneous interfacial reaction of  $\text{In}_{(l)}/\text{Au}_{(s)}$  and  $\text{In}_{(l)}/\text{Cu}_{(s)}$  at  $350^\circ\text{C}$  for 20 min to form the  $\text{Cu}_{11}\text{In}_9$  intermetallic compounds (black particles) and  $\text{AuIn}_2$  intermetallic compounds (gray lumps).

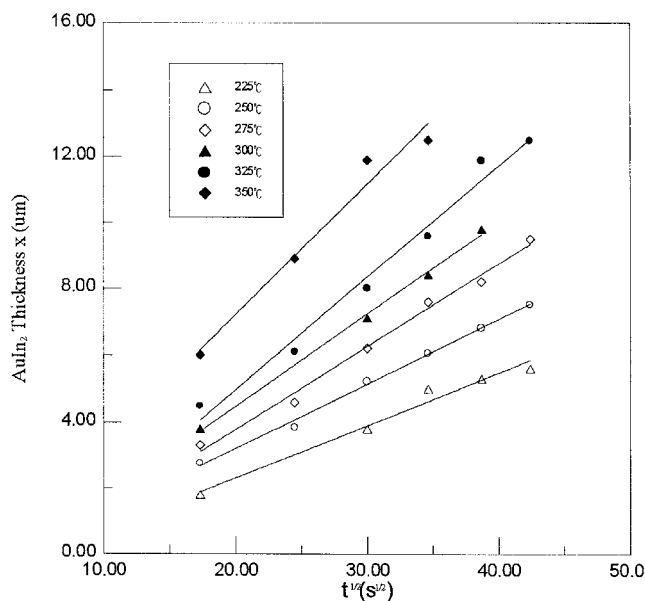


Fig. 6. The thickness of  $\text{AuIn}_2$  intermetallic compound related to the square root of time for the Au/In interfacial reaction.

**Table II. The Logarithmic Exponents and Growth Constants of Intermetallic Compounds Formed during the Au/In Interfacial Reactions**

T ( $^\circ\text{C}$ )	Kp ( $\text{cm}^2/\text{sec}$ )
225	$1.96 \times 10^{-10}$
250	$3.32 \times 10^{-10}$
275	$5.28 \times 10^{-10}$
300	$6.70 \times 10^{-10}$
325	$9.73 \times 10^{-10}$
350	$1.41 \times 10^{-9}$

the solid Au layer, solid-solid interdiffusion between Au and Cu layers occurred simultaneously. However, the reaction rate of the latter, in contrast to that of the former, was too slow to bring about the accumulation of Cu at the In/Au interface above the saturated limit so as to form the  $\text{Cu}_x\text{In}_y$  intermetallic compound. As a

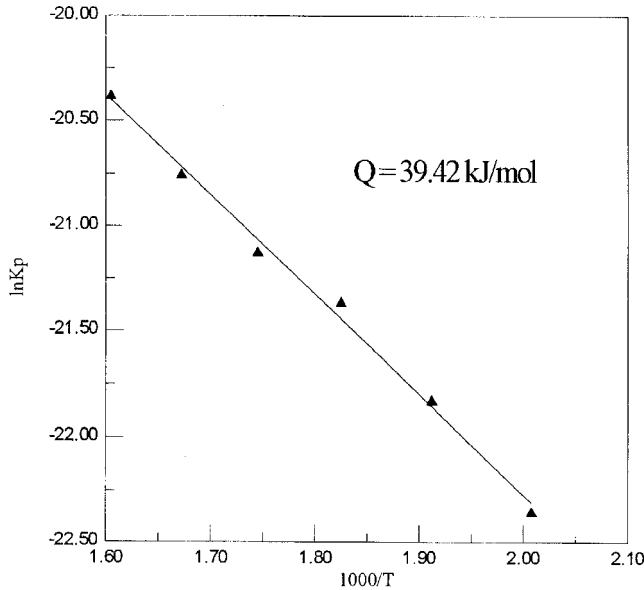


Fig. 7. Arrhenius plot of the growth rate constants ( $K_p$ ) for the Au/In interfacial reaction.

result, the outwardly diffusing Cu atoms continued to dissolve into the  $AuIn_2$  phase. With the increasing of soldering temperature and time, the outward diffusion of Cu atoms accelerated accordingly, resulting in a hike of the Cu content in the  $AuIn_2$  phase. Not until undergoing a prolonged reaction at a relatively higher temperature, did the Au layer reach a nearly exhausted state, enabling a sufficient amount of Cu atoms to react with the In solder. Then, a few of the granular  $Cu_{11}In_9$  compounds began to form, which were embedded in the  $AuIn_2$  particles as shown in Fig. 5.

The measured growth thickness of interfacial  $AuIn_2$  intermetallic compounds ( $\Delta x$ ) corresponding to the square root of the reaction time ( $t^{1/2}$ ) was plotted in Fig. 6, which revealed a linear relation. The deviations of measurements were between 0.2  $\mu m$  and 1.3  $\mu m$ . It indicated that the kinetics of the Au/In interfacial reaction obeyed the parabolic law and the growth of intermetallic compounds was diffusion-controlled. This result was consistent with Jacobson's study on Au/In soldering reactions that the interfacial dissolution would be retarded at the formation of the interfacial  $AuIn_2$  layer.<sup>18</sup> The reaction constants  $K_p$ , defined as  $K_p = \Delta x^2/t$  and prescribed for various soldering temperatures, were given in Table II. The Arrhenius plot of  $K_p$  was shown in Fig. 7, where the activation energy  $Q$  of the intermetallic compound growth was calculated to be 39.42 kJ/mol. The activation energy here was very close to 42.8 kJ/mol for Au diffusion through the  $AuIn_2$  layer into the InSn layer in the Au/InSn reaction, as reported by Shohji.<sup>17</sup>

To evaluate the wettability of liquid indium on Au-deposited substrates, the contact angles were measured by the sessile drop method at various temperatures. The values were plotted as a function of reaction time in Fig. 8. It was found that the contact angles of all specimens declined rapidly to about  $30^\circ$  as the indium cylinders began to melt, and then the curves

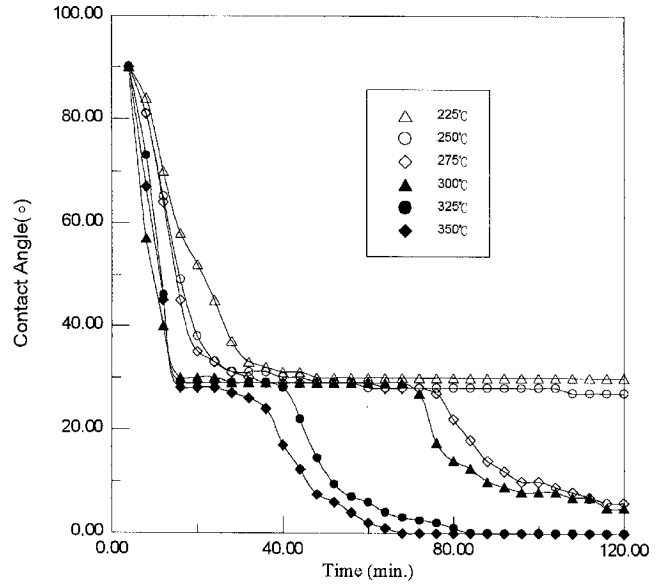


Fig. 8. Plots of contact angles for liquid indium sessile drop wetting on Au deposited substrate versus reaction time at various temperatures.

remained as a plateau for a period of time before they finally collapsed to a very low value. Wang et al.<sup>21,22</sup> also experienced a similar process in their study on the wetting of the PbSn alloy on Cu and Ag substrates. With respect to wetting of the metal surface by liquid solders, which could usually be ascribed to a reacting system, the solder droplets were sometimes observed with halos or precursor films leading the contact line spreading.<sup>23</sup> For example, Kim et al.'s study on the

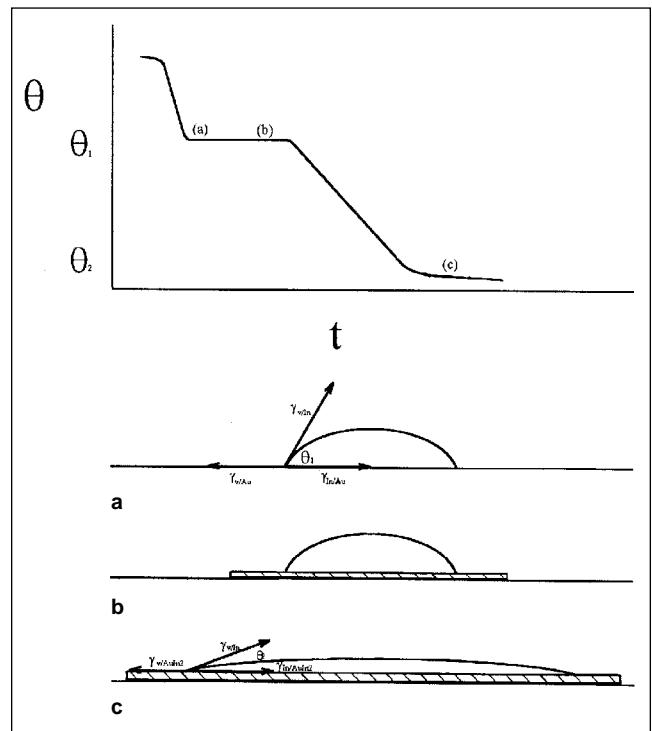


Fig. 9. Schematic presentation of the mechanism of the wetting behavior of indium solder on the Au-deposited substrate: (a) quasi-wetting stage, (b) formation of precursor halo, and (c) final wetting stage.

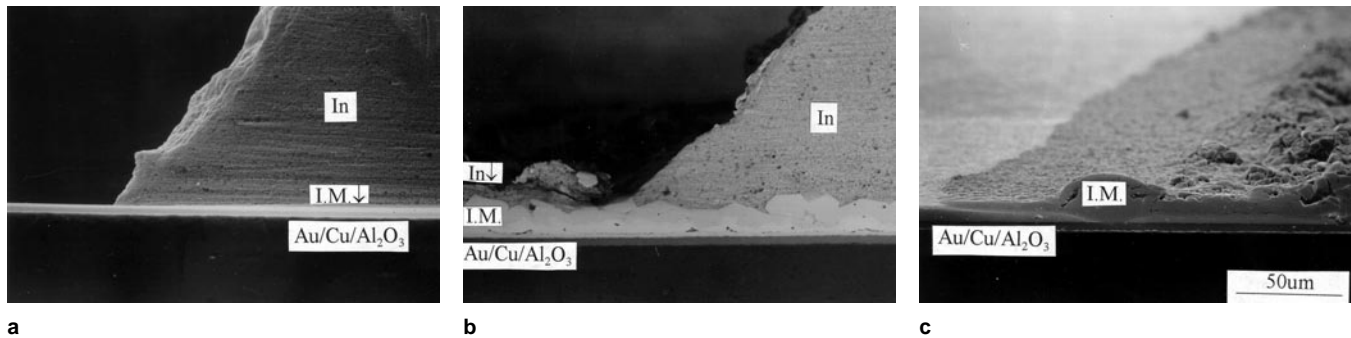


Fig. 10. SEM observations of the wetting behavior of indium solder on the Au-deposited substrate: (a) quasi-wetting stage, 300°C, 3 min; (b) formation of precursor halo, 300°C, 45 min; and (c) final wetting stage, 300°C, 120 min.

wetting of the eutectic PbSn solder on a Cu substrate showed that after the initial spread, the wetting angle remained constant, and the reaction carried on through the formation of intermetallic compounds at the Cu/PbSn interface and the appearance of a band side (halo) surrounding the solder edge.<sup>24</sup> Yost et al. have proposed that the intermetallic compound formation at the interface should exert a more significant influence on the wetting than the driving force of imbalance of the surface tensions in a soldering reaction system.<sup>25</sup> In view of observations made by Wang et al.<sup>21,22</sup> and Kim et al.,<sup>24</sup> and the driving force theory proposed by Yost et al.,<sup>25</sup> a mechanism for the wetting of the In solder on Au-deposited substrates is propounded in this study, as schematized in Fig. 9.

The indium solder melt at the initial stage and resulted in a quasi-wetting contact angle  $\theta_1$  (Fig. 9a). Accompanying the formation of intermetallic compounds at the In/Au interface, some indium atoms spread out of the solder drop through free surface diffusion on Au-deposited substrates. As these outspreading indium atoms could diffuse farther away from the edge of the liquid drop and accumulate to a critical thickness, reaction with the Au surface would occur, and a precursor halo would thereby appear (Fig. 9b). The formation of intermetallic precursor halos caused the surface tension of the vapor/substrate ahead of the indium solder drop to vary from  $\gamma_{V/Au}$  to  $\gamma_{V/I.M.}$ . Also, the surface tension of the solder/substrate interface would change from  $\gamma_{In/Au}$  to  $\gamma_{In/I.M.}$ . The change of surface tensions resulted in the drastic decrease of the contact angle to  $\theta_2$  (Fig. 9c). This mechanism was brought to light through SEM observations of the cross-sections of specimens after wetting tests, as shown in Fig. 10, where three stages of the wetting process corresponding to those described above in the proposed mechanism (Fig. 9a, b, and c) were clearly delineated.

## CONCLUSIONS

In the soldering process of liquid indium with Au-deposited substrates in the temperature range of 225°C to 350°C, the intermetallic compound AuIn<sub>2</sub> is found to appear in two continuous wavy and floating-island forms. The growth kinetics of AuIn<sub>2</sub> follows the parabolic law, which indicates that the reaction is diffusion-controlled and the activation energy is

39.42 kJ/Mole. The wetting tests in the temperature range between 225°C to 375°C show that the contact angle of liquid indium on Au-deposited substrates declines rapidly to about 30° at the initial stage, and then remains constant for a period of time before finally collapsing to a very low value. For the interpretation of such a wetting behavior, a mechanism has been proposed, which is based on the formation of precursor halos ahead of the liquid indium drop. Through SEM observations of the cross-sections of the specimens after wetting tests, three stages of the wetting process in the proposed mechanism can be clearly ascertained.

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