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Article in Journal of Materials Science Materials in Electronics - June 2018

DOI: 10.1007/s10854-018-9410-8

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Comparative study of interfacial interaction between aromatic and aliphatic functional group in solder wettability

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Received: 30 November 2017 / Accepted: 1 June 2018
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Abstract
The effect of using different flux on wettability of Sn-Ag-Cu lead free solder were investigated. In this study, solder paste Sn-3.0Ag-0.5Cu (SAC305) was used by introducing two types of no-clean flux with different ingredients. The solders namely as SAC305-A and SAC305-B respectively. Then, the both solder paste manually printed on printed circuit board (PCB) using stencil printing and then reflowed at 260 °C temperature. Wettability of Sn-Ag-Cu solder using different flux was determined by contact angle measurement using Alicona ® IFM software. Results show the SAC305-A solder alloys have a good and better wettability with lower contact angle compared to SAC305-B. Functional groups of both solder flux was identified by FTIR analysis. Meanwhile XPS analysis was performed in characterizing the studied fluxes. It was found that no-clean flux solder with aromatic functional groups showed lower contact angle value and better wettability than aliphatic contained functional groups.

1 Introduction
In advent soldering technology, fluxes have always played a vital role in solder paste by providing necessary support to ensure solderability. But what actually its main role and does it have more crucial functionality than just to ensure uniform mixture of the solder paste? Contact angle which is commonly employed to determine wettability of solder is closely related to the surface tension of the molten solder on Cu substrate during the soldering process. Changing of surface tension by using different flux ingredients or contents influences the contact angle and indirectly affects the wettability of solder alloy [1]. Previous researcher reported that using of different flux types such as with high and low acid contents, different activator and surfactant has affected the wettability of solder [2–5]. Mario and co-workers [6], reported that with the use of rosin mild activator (RMA) flux, it lowered the contact angle value ranging from 10° to 30° compared to rosin activator (RA) and rosin (R) types of flux ranging from 20° to 30° and 35° to 60° respectively. In addition, Wu and co-workers [7], revealed only rosin activator (RA) flux provided a sufficient wetting for Sn-Zn-RE solder alloys compared to RMA, R and VOC-free fluxes.

Due to that scenario, the actual content and composition of ingredients in fluxes are not commonly known. Hence, the actual role of each ingredient cannot be identified but one thing known is that different fluxes will provide different level of wetting that contributes to the adhesion of the solder on the substrate. It is our intention to investigate solderability by mean of contact angle using two commercially available fluxes: denoted as flux A and flux B to form a solder paste namely as SAC305-A and SAC305-B respectively. We aspire that these findings could contribute to the understandings of flux functionality on top of its main role, which lead to a more well-versed decision in choosing fluxes for specific applications. Furthermore, inadequate report on the role and mechanism of functional groups in flux in contributing to the
solderability has spurred our interest in relating fundamental studies in interfacial interaction of solder joints.

2 Experimental procedure

2.1 Soldered samples

Solder powder Sn-3.0Ag-0.5Cu (SAC 305) with size range of 35 to 20 µm was incorporated by flux A and flux B to produce SAC305-A and SAC305-B solder alloys respectively. Fabrication of solder paste included raw materials (solder powder and flux) was carried out by Red Ring Solder (Malaysia) Sdn. Bhd. Soldered samples were prepared by manually printing of solder paste onto printed circuit board (PCB) with copper (Cu) surface finish using stainless steel stencil printing. Then, the printed solder pastes were reflowed at peak temperature of 260 °C in a reflow soldering oven. Same sizes of soldered samples with the length of 5.0 mm were cut into a small piece by a diamond cutter. Figure 1 shows the soldered PCB and size of catted sample take out for this experiment. Samples were cold mounted using a mixture of resin prior to grinding and polishing.

2.2 Contact angle measurement

Upon solidification during the reflow soldering, all samples exhibited a spherical-cap shape. Therefore the degree of angle between the solder sphericap-cap shape and Cu substrate was measured after it solidified. Contact angle of polished samples were examined using Alicona ® Infinite Focus Measurement (IFM). By using image processing software via IFM, contact angle of samples were measured as shown in Fig. 2. Five measurements were taken for each sample and average of contact angle values were represented by the θ. This method previously used by Guo and co-workers [8], for determining contact angles.

Contact angle is commonly used to determine the wettability of solder on the Cu substrate and it is closely related to the surface tension of the molten solder on Cu substrate during the soldering process. It can be explained by the Young-Dupre law for solder-flux-copper system as below [9].

\[
\cos \theta = \frac{\gamma_{sf} - \gamma_{sl}}{\gamma_{lf}}
\]

where \( \gamma_{sf} \) is a surface tension of substrate-flux, \( \gamma_{sl} \) is a surface tension of substrate-liquid solder and \( \gamma_{lf} \) is a surface tension of liquid solder.
tension of liquid-flux. According to that law, imbalance of the surface tension at the solder/flux/substrate triple joint is the driving force for the spreading of the solder. An increase in $\gamma_{sf}$ or decrease in $\gamma_{lf}$ will decrease the contact angle, thus increase the wettability.

### 2.3 FTIR and XPS

Different functional groups of investigated solder were analyzed by Fourier transform infrared spectroscopy (FTIR) using Perkin Elmer Spectrum 400 FT-IR. Binding energy and broadening phenomenon of solder alloys were studied using X-ray Photoelectron Spectroscopy (XPS), model Kratos Axis Ultra DLD. For FTIR and XPS, solder paste prior to soldered samples were taken for analysis.

### 3 Result and discussion

Table 1 show the average contact angle values ($\theta$) of SAC305-A and SAC305-B solder alloys after reflow soldering. Contact angle value ($\theta$) of SAC305-B (30.4°) was higher compared to SAC305-A (25.6°). Micrograph of measured contact angle for both solder indicated in Fig. 3. The values of $\theta$ could represent the wetting quality and it reflects the solderability of the materials. Contact angle which is in a range of $0^\circ < \theta < 30^\circ$ shows a very good wetting; $30^\circ < \theta < 40^\circ$ is a good wetting; $40^\circ < \theta < 55^\circ$ is an acceptable; $55^\circ < \theta < 70^\circ$ is poor wetting and $> 70^\circ$ is low wetting. The smaller value of $\theta$ the better both wettability and solderability [10–12]. According to the present work, SAC305-A was considerably possessed better wettability compared to SAC305-B. Different wettability properties between SAC305-A and SAC305-B were related to the use of different flux ingredient or content. Wettability of solder on Cu substrate was categorized as reactive wetting.

### Table 1 Contact angle of SAC305-A and SAC305-B solder

<table>
<thead>
<tr>
<th></th>
<th>SAC305-A</th>
<th>SAC305-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average contact angle ($\theta$)</td>
<td>25.6°</td>
<td>30.4°</td>
</tr>
</tbody>
</table>

Interestingly, the current finding showed aromatic functional groups appeared in the flux systems which seemed to induce the strong adhesion between molten solder and Cu substrate, thus improved the wettability of solder alloys. In contrasts, the flux associated with an aliphatic functional group has significantly higher contact angle value ($\theta$) of 30.4° compared to aromatic functional group of 25.6°. FTIR analysis of both investigated solders was illustrated in Fig. 4. A summary of detected functional groups were presented in Table 2. According to the FTIR analysis, three different peaks can obviously be seen for SAC305-A which were clearer than SAC305-B solder. Those peaks which detected at absorption band of 3304, 1539 and 1418 cm$^{-1}$ were known as secondary amine, alkenyl and aromatic carbon chain respectively (mark as red circle in FTIR spectrum). Existence of three different functional groups in SAC305-A solder were attributed to the incorporation of flux A. These functional groups of SAC305 incorporated by Flux A were considerably more significant in reducing the contact angle and provided greater effect on wettability as compared to SAC305 incorporated by flux B.

In this study, existence of three functional groups in flux A, known as secondary amine, alkenyl and aromatic were effective to decrease the surface tension of SAC305-A, thus promoted fast spreading of molten solder and reduced the contact angle. Flux was mainly introduced during soldering.
in order to remove the oxide film on Cu substrate and prepare clean surface for molten solder to wet and to be joint [13, 14]. Chemical reaction of flux with metal oxide might be explained according to Bronsted/Lewis acids theory. Based on this theory, active acid species which is acidic flux acts as a donor of proton and base metal Cu acts as a proton acceptor. Reaction of flux and metal oxide induced the formation of salt and water. Formed salt reacts as surfactant which increases the surface tension of molten solder [15]. Generally, carboxylic acid is the main active species in the flux and it was indicated by FTIR spectrum in both investigated solders. Presence of functional groups included secondary amine, alkene and aromatic act as activator which significantly assist and boost the fluxing activity. According to the current finding, chemical reaction of flux A (containing aromatic and aliphatic chains) and flux B (containing only aliphatic chain) with the metal oxide was proposed respectively as below:

### 3.1 Flux A

\[
\text{Metal oxide} + \text{Carboxylic acid} + [\text{secondary amine} + \text{alkenyl} + \text{aromatic}] \\
\text{CuO} + 2\text{RCOOH} + \text{C}_2\text{H}_3\cdot\text{NH}\cdot\text{C}_6\text{H}_6 = \text{Cu (RCOO)} + \text{C}_2\text{H}_3\cdot\text{NH}\cdot\text{C}_6\text{H}_6 + \text{H}_2\text{O}
\]
### 3.2 Flux B

Metal oxide + Carboxylic acid

\[
\text{CuO} + 2\text{RCOOH} = \text{Cu} (\text{RCOOCH}_2) + \text{H}_2\text{O}
\]

Formed salt from the chemical reaction flux and metal oxide interacted with the metal cations from solder. The presented cations were Sn\(^{2+}\), Ag\(^{2+}\) and Cu\(^{2+}\). This interaction drove the molten solder to spread on the Cu substrate surface. Existence of the aromatic functional group in flux A produced the cation-π interaction. This interaction was classified as a non-covalent molecular interaction between the face of an electron-rich π system (e.g. benzene, ethylene, acetylene) and adjacent cation. This interaction was an example of non-covalent bonding between a monopole (cation) and a quadrupole (π system). It was found that interaction energies of cation-π pairs correlated well with electrostatic potential above and below the aromatic face structure [16–18].

Figure 5 illustrates the schematic of metal cation-π interaction that was suggested for Sn-Ag-Cu molten solder and formed salt of the flux. As compared to aliphatic chain, the aromatic chain has a quadrupole charge distribution. Benzene for example, has electron-rich π system above and below the benzene ring host a partial negative charge. A counterbalancing positive charge is associated with the plane of the benzene atoms, resulting in an electric quadrupole (a pair of dipoles, aligned like a parallelogram so there is no net molecular dipole moment). Consequently, the negatively charged region of the quadrupole can interact favorably with positively charged species; a particularly strong effect is observed with cations of high charge density [19, 20].

Besides that, the substituent electronic properties of aromatic chain affect the strength of the cation-π interaction. Existence of secondary amine which is electron donating substituents strengthens the cation-π interaction [21, 22]. Therefore, stronger cation-π interaction that was induced by Flux A than Flux B tended to decrease the surface energy of molten solder and decrease the surface tension of solder. On the other hand, intermolecular interaction of aromatic system and metal cation creates a stronger adhesion

![Fig. 5 Schematic representation of aromatic interaction involving cation-π interaction](image)

#### Table 3

<table>
<thead>
<tr>
<th></th>
<th>Sn 3d peak binding energy (eV)</th>
<th>Full width at half maximum (FWHM) (eV)</th>
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<tbody>
<tr>
<td>SAC305-A</td>
<td>487.40</td>
<td>1.480</td>
</tr>
<tr>
<td>SAC305-B</td>
<td>487.16</td>
<td>1.413</td>
</tr>
<tr>
<td></td>
<td>(\Delta = 0.12)</td>
<td>(\Delta = 0.067)</td>
</tr>
</tbody>
</table>

![Fig. 6 XPS spectrum of Sn peaks for a SAC305-A solder, b SAC305-B solder](image)
between molten solder and Cu substrate as compared to the cohesion of the solder itself [23]. Therefore, the wettability of the solder was improved and the contact angle was reduced. As reported by Liu and co-workers [24], wettability of nano composite Sn-Ag-Cu solder reinforced by graphene was improved with the presence of non-polar interaction between resin flux containing abietic acid which have an aromatic ring with the graphene. The existence of aromatic ring attracted graphene to the substrate surface, lowered the surface tension and increased the wettability of nano composite solder [24].

XPS analysis of Sn3d peaks for SAC305-A and SAC305-B was indicated in Fig. 6. Details of binding energy of Sn for both solder were listed in Table 3. Binding energy of SAC305-A was slightly higher than binding energy of Sn in SAC305-B solder. The binding energy shifted about 0.12 eV compared to Sn in SAC305-B solder. The shifted binding energy was substantially related to the interaction of Sn nucleus with electron at core level. The shifted binding energy towards higher position signified that Sn withdrew the electron thus, interaction of nucleus with the presence of electron became stronger. In this case, the existence of aromatic structure in flux A (for SAC305-A) provided a strong attraction to the Sn ion and more electrons in Sn were attracted to the aromatic structure resulted in a formation of cation-π interaction.

The occurrence of strong interaction was indicated by broadening of full width at half maximum (FWHM) peaks of Sn in SAC305-A. The broadened of FWHM Sn peak for SAC305-A is about Δ = 0.067 eV [25]. Particularly, the overall Gaussian broadening suggested a statistical variation in electronic and geometric structures of the supported clusters associated with a multitude of different adsorption sites, coordination numbers and cluster-surface interaction strength [26]. The broadening of Sn peaks in SAC305-A was attributed to the chemisorption influenced by cation-π interaction.

4 Conclusion

Effect of using different flux towards wettability of Sn-Ag-Cu solder was investigated. Wettability properties of SAC305-A and SAC305-B were determined by measurement of contact angle. Contact angle of Sn-Ag-Cu using flux A (SAC305-A) showed the lower value (25.6°) compared to Sn-Ag-Cu using flux B (SAC305-B) (30.4°). Better wettability of SAC305-A was due to the existence of aromatic, alkenyl and secondary amine functional groups in flux A. Presence of these three functional group provided a special effect which was significantly induced strong non-polar interaction that contributed in decreasing the surface tension of SAC305-A solder. In commercial practice, the idea behind putting different functional groups was proposed to make a full usage of these group characters. Existence of functional groups with high density of electron or high electronegativity such as aromatic, alkenyl and secondary amine induced strong non-polar interaction between cation and anion which significantly improved the adhesion and wettability of solder joint.

Acknowledgements The authors gratefully acknowledge the financial support of this work from Ministry of Higher Education of Malaysia through My Brain 15 PhD scholarship programme and Universiti Kebangsaan Malaysia (UKM) for research grants GGPM-2017-048 and DPP-2015-042.

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