マテリアル先端リサーチインフラ利用報告書
ARIM User's Report

【Release：2024.10.22】　【Update：2024.10.22】

課題データ / Project Data

項目	内容
課題番号 Project Issue Number	22KU0046
利用課題名 Title	In-situ high voltage transmission electron microscope study of the intermetallic compounds (IMCs) formed between Ga-based alloys and Cu-based substrates.
利用した実施機関 Support Institute	九州大学 / Kyushu Univ.
機関外・機関内の利用 External or Internal Use	外部利用/External Use
横断技術領域 Cross-Technology Area	計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	マテリアルの高度循環のための技術/Advanced materials recycling technologies 次世代ナノスケールマテリアル/Next-generation nanoscale materials
キーワード Keywords	Low temperature solder, Gallium, intermetallic compounds (IMCs), transmission electron microscopy

利用者と利用形態 / User and Support Type

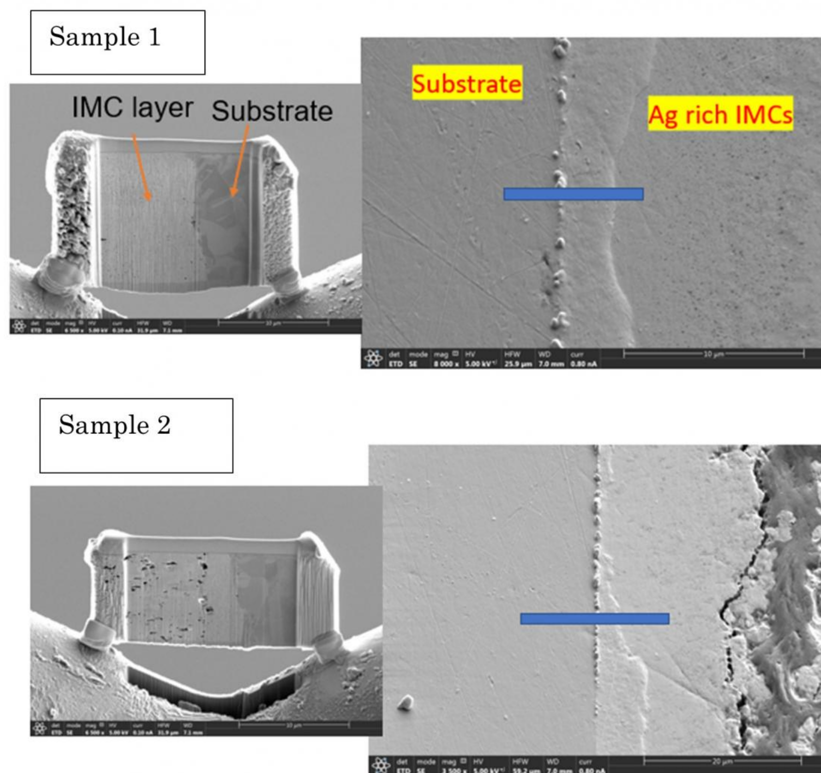
項目	内容
利用者名（課題申請者） User Name (Project Applicant)	Kazuhiro Nogita
所属名 Affiliation	The University of Queensland Mechanical and Mining Engineering
共同利用者氏名 Names of Collaborators in Other Institutes Than Hub and Spoke Institutes	Xin Fu Tan,Qichao Hao
ARIM実施機関支援担当者 Names of Collaborators in The Hub and Spoke Institutes	Kazuhiro Yasuda,Hiroshi Maeno
利用形態 Support Type	技術補助/Technical Assistance

利用した主な設備 / Equipment Used in This Project

項目	内容
利用した主な設備 Equipment ID & Name	KU-001：電子分光型超高圧分析電子顕微鏡

報告書データ / Report

概要（目的・用途・実施内容） Abstract (Aim, Use Applications and Contents)	The requirement to reduce soldering temperature for lower power consumption, lower costs and environmental friendly processing has attracted wide attention among the electrical packaging industry. To decrease the soldering temperature, liquid Ga is a promising candidate due to its near room temperature melting point of 29.76℃ and non-toxic property. Liquid Ga can react with the Cu substrate to form a solid solder joint by forming intermetallic compounds like $CuGa_2$ and Cu_9Ga_4 with solidus temperatures of 254℃ and 466℃ . However, the formation of intermetallic compounds (IMCs) between Ga with Cu substrate, which is conventional substrate in electronic devices, is slow limiting the application of Ga based soler alloys. This research proposed a new method for accelerating the formation of the IMCs layer by electrically plating a layer of Ag on the Cu based substrate. The results show that the IMCs layer is much thicker after introducing an Ag layer compared to pure Cu based substrate. Therefore, this method is worth detailed investigation of both morphology and phases of the IMCs layer and to check the stability of these IMCs. These can provide information the further improvement. Therefore, the aims of this experiment are: ・ To study the morphology of phases at the substrate interface and to identify the phases formed between GaSn or Ga and the substrate when a layer of electrically plated Ag is present between the solder and the substrate. ・ To study the morphology change of the IMCs during heating from 30℃ to 260℃ (20℃ every step). ・ To study the diffraction patterns of the IMCs phases from 30℃ to 260℃ (20℃ every step).
実験 Experimental	1.1 Sample fabrication:The intermetallic joints between couples of Ga/Cu(Ag plated), Ga13.5 wt%Sn/Cu(Ag plated) and Ga/Cu6Ni(Ag plated) were fabricated at 150ºC for 2h. The excess Ga/Ga13.5%Sn were removed by 10% HCl. The samples were mounted in resin and polished before a focused ion beam (FIB) technique was used for preparing the high voltage transmission electron microscopy (HV-TEM) lamellar samples. All FIB samples’ thickness is controlled as 500nm.The Sample 1 and Sample 2： Sample 1 and Samples 2 are Ga13.5wt%Sn/Cu(Ag), and the interface between the substrate and the IMC layer were selected for preparing the TEM samples (Fig.1). Sample 3 Sample 3 is Ga/Cu(Ag), and the interface between the substrate and the IMC layer was selected for preparing the TEM sample (Fig.2). Sample 4 and Sample 5:Sample 4 and Sample 5 were cut from the Ga/Cu6Ni(Ag) interface at two different areas. Sample 4 is from the edge reaction area where Ga was fully consumed during the reaction with the substrate, and Sample 5 is from an area with excess Ga (Fig.3). 1.2 In-situ heating high voltage transmission electron microscopy (HV-TEM)The samples were placed on a heating TEM holder. Sample 1 of Ga13.5wt%Sn/Cu(Ag), Sample 3 of Ga/Cu(Ag), and Sample 5 of Ga/Cu6Ni(Ag) were heated from 30℃ to 200 ℃. Images and diffraction patterns were taken every 20℃. The microstructure and diffraction patterns of Sample 2 Ga13.5wt%Sn/Cu(Ag) and Sample 4 of Ga/Cu6Ni(Ag) were checked at room temperature before and after heating to 200℃.

結果と考察 Results and Discussion	The researchers conducted experiments by taking images and diffraction patterns of the interface of the samples at different temperatures ranging from 30 ℃ to 200 ℃ with a 20℃ interval. The Ga/Cu(Ag) couple was the easiest system for these experiments and it consists of three main layers: Cu substrate, Cu-rich IMC layer, and Ag-rich IMC layer (Fig.4). It was confirmed that all plated Ag had reacted and formed a layer of IMCs above the Cu-rich IMC layer, and this Ag IMCs layer appeared to be more porous than the Cu-rich IMC layer. As the heating began, each IMC layer was observed to examine changes in morphology and phase transformation. It was found that the morphology of the phases remained relatively stable before the temperature reached 160 ℃. Fig.4 illustrates the morphology of the whole Sample 3 Ga/Cu(Ag) at different temperatures, including 40℃, 140 ℃, at the beginning of 160℃, holding at 160℃ for a while, at the beginning of 180℃, and holding at 180 ℃ for a while. The IMC layer near the Cu substrate side remained stable before 160℃, and the Cu_9Ga_4 layer began to grow at 160℃ between the Cu substrate and the IMC layer interface. At 180℃, the Cu_9Ga_4 layer at the interface between the Cu-rich IMC layer continued to grow, and the morphology of the Ag-rich IMC layer also changed. It was observed that some Ag-rich IMCs appeared to have dissolved, leaving thin film areas like cavities. For the Cu6Ni(Ag)/Ga sample, the same phenomenon was observed at 160℃, that the Cu_9Ga_4 IMC layer at the interface began to grow significantly and Ag IMCs dissolved when temperature is high (Fig.5). The phase transformation phenomenon was also found for the Ga13.5wt%Sn/Cu(Ag) system. After introducing Sn into the system, the composition of the IMCs become more complicated and further EDS and XRD experiments will be combined with these HV-TEM results to confirm the phases.
図・表・数式 1 Figures, Tables and Equations 1	 Fig.1 Sample 1 and Sample 2 of Ga13.5wt%Sn /Cu(Ag) 150ºC 2h.

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<td>図・表・数式 2
Figures, Tables and Equations 2</td>
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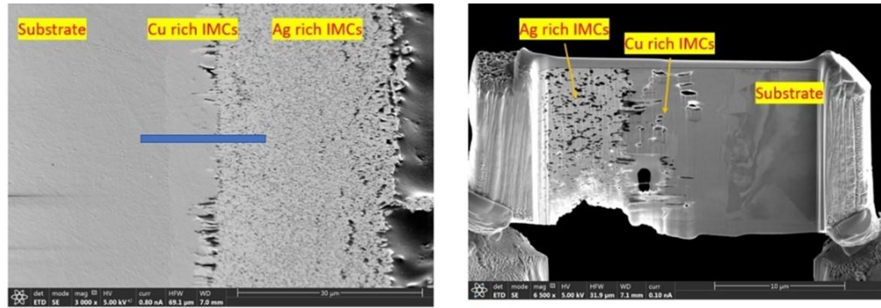

Fig.2 Sample 3 of Ga/Cu(Ag) 150ºC 2h.

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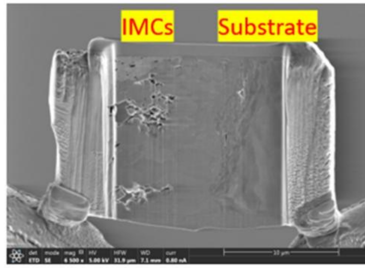
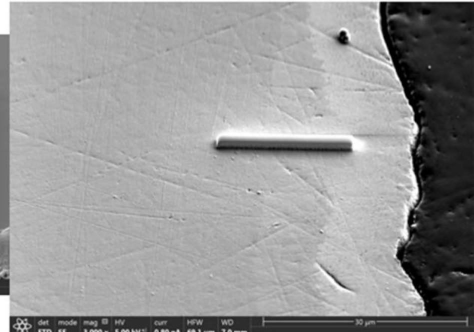
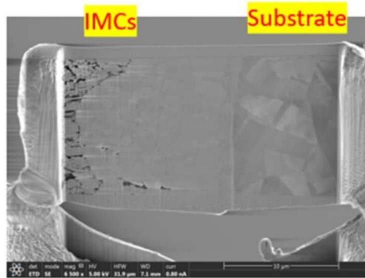
Sample 4





Sample 5



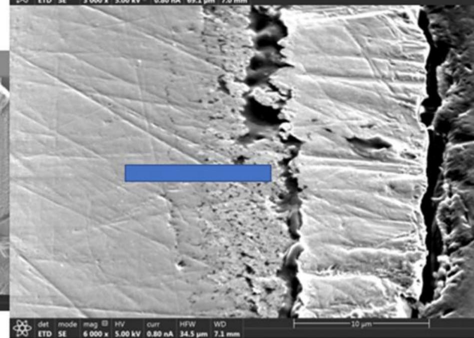


Fig.3 Sample 4 and Sample 5 of Ga/Cu6Ni(Ag) 15º0C 2h.

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図・表・数式 4 Figures, Tables and Equations 4	Fig.4 Morphology change of Sample 3 of Ga/Cu (Ag).
図・表・数式 5 Figures, Tables and Equations 5	Fig.5 Morphology change of Sample 5 of Ga/Cu6Ni (Ag).
その他・特記事項（参考文献・謝辞等） Remarks(References and Acknowledgements)	Funding: This work was supported by The University of Queensland, Australia [Knowledge Exchange & Translation fund 2021002690]; Nihon Superior Co., Ltd, Japan [2016001895, 2021002341]; Australian Research Council, Australia [LP180100595]; and Walter and Eliza Hall Travelling Scholarship.

成果発表・成果利用 / Publication and Patents

DOI（論文・プロシーディング） DOI (Publication and Proceedings)	
口頭発表、ポスター発表および、その他の論文 Oral Presentations etc.	
特許出願件数 Number of Patent Applications	0件

特許登録件数 Number of Registered Patents	0件