PREFACE

This thesis is submitted for the degree of Doctor of Philosophy in Mechanical Engineering at the National University of Singapore. The research described herein was conducted under the supervision of: (i) Associate Professor Manoj Gupta from the Materials Science Division, Department of Mechanical Engineering, National University of Singapore (NUS), (ii) Dr. Wei Jun from the Micro-joining and Substrate Technology (MST) group, Singapore Institute of Manufacturing Technology (SIMTech) and (iii) Dr. Wu Ping from the Computational Materials Science and Engineering group, Institute of High Performance Computing (IHPC), between January 2004 and Dec 2007.

This work is to the best of my knowledge original, except where acknowledgements and references are made to previous work. Neither this, nor any substantially similar thesis has been or is being submitted for any other degrees or other qualification at any other university. This thesis contains no more than 40,000 words.

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Summary

For several decades, tin-lead solders have been extensively used as interconnect materials. However, through the years, to cater to the ever-increasing technological changes, the number of solder joints per package has increased while the dimensions of the solder joints have decreased. Furthermore, coupled with environmental concerns over the toxicity of lead and legislative implementation to ban the use of lead in electronics manufacturing, there is a need to move beyond tin-lead solders. The primary focus is to develop a new generation of interconnect materials that is equipped with a combination of good mechanical, electrical and thermal properties, in order to fulfill the ever-stricter service requirements.

In this project, a new generation of lead-free (95.8Sn-3.5Ag-0.7Cu) composite solders was developed to address the above-mentioned issues. Composite approach was used to improve the service performance of conventional solders. This project was carried out in three phases. In Phase One, four new lead-free composite solders were successfully synthesized using the powder metallurgy method. Non-coarsening reinforcements (carbon nanotubes, TiB_2, Y_2O_3 and ZrO_2 + 8mol. % Y_2O_3 particulates) were intentionally incorporated into the solder matrix. Characterization studies were then carried out to determine the physical, electrical, thermal, microstructural and mechanical properties of the composite solders. Composite solders reinforced with carbon nanotubes (CNTs) were found to yield the best overall properties. Phase Two of this project focused on creep and aging studies of Sn-Ag-Cu/CNT composite solder joints. In the last phase of this project, a computational study involving the adsorption energy calculations for Sn-CNT system was

carried out. This was aimed to understand the interfacial interaction between Sn and CNT, so as to maximize the potential of CNTs as reinforcement in the solder matrix.

Characterization results in this project convincingly established that composite technology in electronic solders can lead to simultaneous improvement in thermal performance (in terms of lower coefficient of thermal expansion) and mechanical performance (in terms of better microhardess, tensile, shear and creep properties), without compromising on the melting temperature and electrical performance (in terms of no change in electrical resistivity/conductivity). A threshold addition of reinforcements was observed to aid in optimizing the properties of the composite solder. Isothermal aging studies revealed that SnAgCu/CNT composite solder joints exhibited lower diffusion coefficient, signifying that the presence of reinforcements was effective in retarding the interfacial intermetallic layer growth. These advanced interconnect materials will hence benefit the microelectronics packaging and assembly industry.

Computational results predicted weak interaction between Sn and its neighboring C atoms. The computational results are also in good agreement with the experimental TEM study. Moreover, TEM study showed that in spite of the weak interaction, the interface integrity between the Sn metal and CNT was generally good. No voids/debonded regions were observed at the Sn/CNT interface.

Particular emphasis was also placed to establish the relationship of varying amount of reinforcements, with the properties of the resultant composite solders.

LIST OF FIGURES

LIST OF TABLES

Publications

Below is a list of references where part of the results from this thesis has been published in international journals and presented at international conferences.

International Journal Publications

1. S. M. L. Nai, M. Gupta and J. Wei, Development of Novel Lead-free Solder Composites using Carbon Nanotube Reinforcements, *International Journal of Nanoscience*, 4 (4), 423 – 429, 2005.

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5. S. M. L. Nai, J. Wei and M. Gupta, Effect of Presence of Multi-walled Carbon Nanotubes on the Creep Properties of Sn-Ag-Cu Solder, *In Proc. ASME IMECE 2006*, 5^{th} – 10^{th} November 2006, USA.

6. S. M. L. Nai, M. Gupta and J. Wei, Influence of Temperature on the Creep Properties of Sn-Ag-Cu Solder Reinforced with Multi-walled Carbon Nanotubes, *In Proc. International Conference of Materials for Advanced Technologies (ICMAT 2007)*, Symposium H, 1^{st} – 6^{th} July 2007, Singapore.

7. S. M. L. Nai, J. Wei and M. Gupta, Influence of Reinforcements on the Electrical Resistivity of Novel Sn-Ag-Cu Composite Solder, *In Proc. ASME IMECE 2007*, 11^{th} – 15^{th} November 2007, USA.

8. S. M. L. Nai, M. Gupta and J. Wei, Suppressing Intermetallic Compound Growth in SnAgCu Solder Joints with Carbon Nanotubes Addition, *IEEE International Nanoelectronics Conference (INEC) 2008*, 24^{th} – 27^{th} March 2008, Shanghai, China.

Poster Presentations

1. S. M. L. Nai, M. Gupta and J. Wei, Enhancing the Properties of a Lead-free Solder Using Carbon Nanotubes as Reinforcement, *MRS-S National Conference on Advanced Materials*, 6th August 2004, Singapore.

2. S. M. L. Nai, J. Wei and M. Gupta, Effect of Presence of Different Reinforcements on the Properties of Sn-Ag-Cu Solder, *2nd MRS-S National Conference on Advanced Materials*, 18th – 20th January 2006, Singapore.

3. S. M. L. Nai, J. Wei and M. Gupta, Effect of Ceramic Reinforcements on the Wettability and Electrical Resistivity Properties of SnAgCu Solder Composites, *Surface Engineering for Industrial Applications (SEIA 2006),* 5th – 7th December 2006, Singapore. ***(Awarded Best Student Poster)***