Pb-Free Nanosolder Project

Ning Cheng Lee

Productronica

November 15, 2007

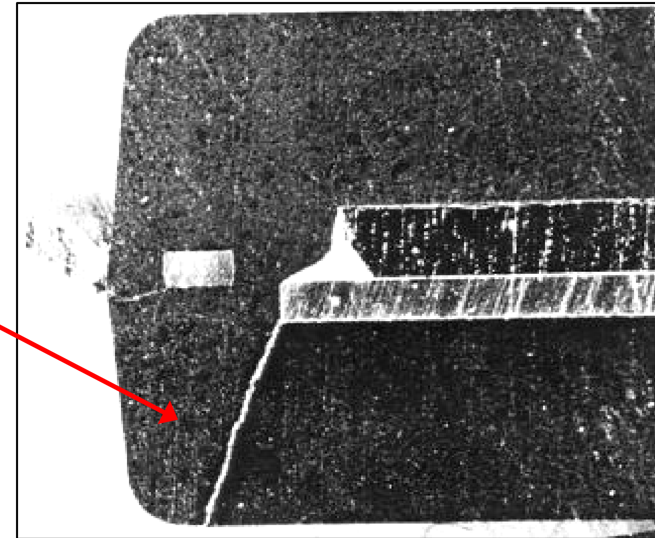
Advancing manufacturing technology

A New Reflow Technology

- The Sn/Ag/Cu based solders have higher bulk melting points than traditionally used Sn/Pb solders

- High reflow temperatures can lead to microelectronic component damage during production

- Lower reflow temperatures make other technologies possible:
    - More fragile, ultra low-K dielectrics
    - Higher performance, less temperature tolerant materials

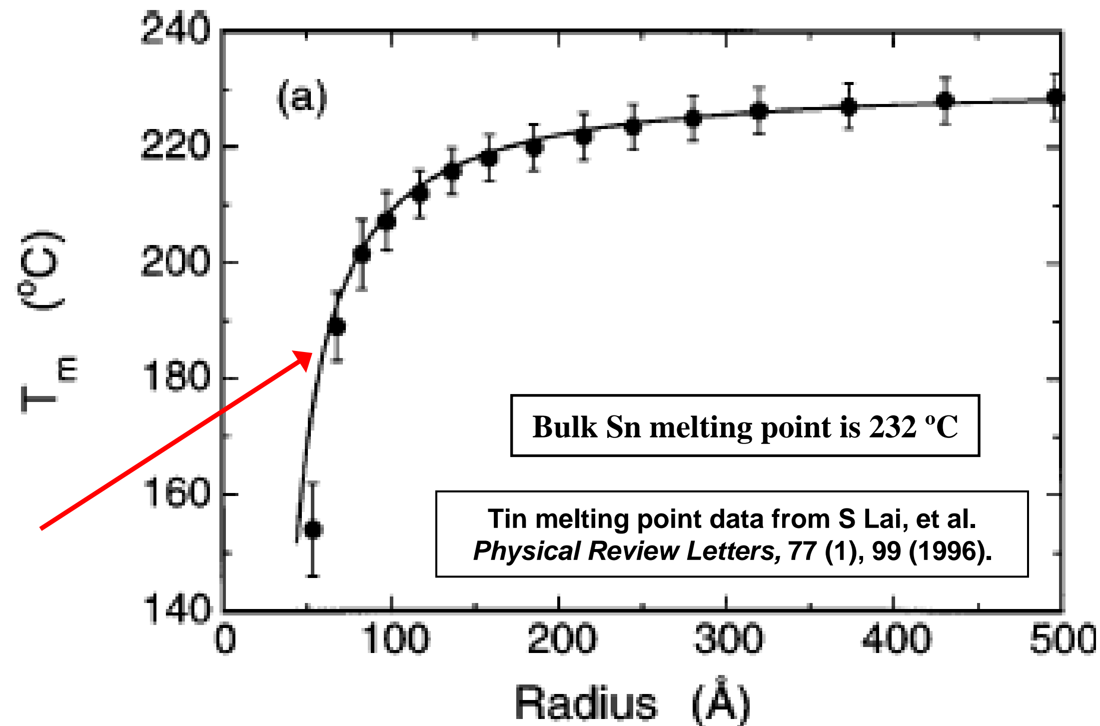


Richard Parker, IEEE, *iNEMI Pb-Free Solder*, "Impact of Elevated Reflow Temperatures on Component Performance," Wiley Press, Editors, Jasbir Bath, Edwin Bradley, Carol Handwerker, 2006 (in press)

So how can Pb-free solders be processed such that their melting point is lowered without undermining solder joint properties?

A New Reflow Technology

- Use melting point depression due to the thermodynamic size effect observed for nanoparticles.
    - **Melting point decreases with decreasing particle size.**
- A melting point near or below 183 ^{0}C is desired. In pure tin this corresponds to a particle size of ~15 nm.



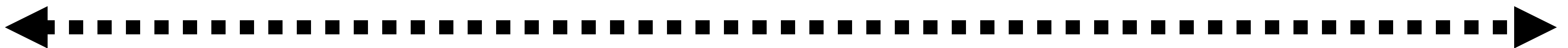
"**Pb-free nanosolder**" made up of solder alloy nanoparticles may be a viable solution and will offer other phenomenal manufacturing advantages.

iNEMI NanoSolder Project

Key players are involved – from the beginning

Chemists + Materials Scientists + Technologists

Raw Material Suppliers + Paste Suppliers + Final Users (EMS + OEMs)



iNEMI NanoSolder Project

Motorola: Andrew Skipor, Project Champion

MetaMateria Partners: Suv Sengupta, Rao Revur

Purdue University: Carol Handwerker, Kevin Grossklaus, Eric Stach, John Koppes

Indium Corporation: Hong-Sik Hwang, Ning-Cheng Lee

Delphi Electronics and Safety: Rich Parker

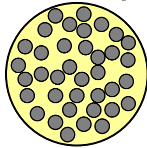
Celestica: Polina Snugovsky

Nanodynamics: Alan Rae

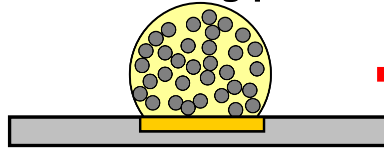
National Institute of Standards and Technology

Nanosolder: New Technology/New Opportunities

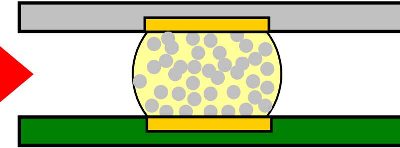
Nanosolder needs a homogeneous and high metallic particle concentration (>85 wt%)

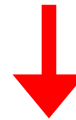


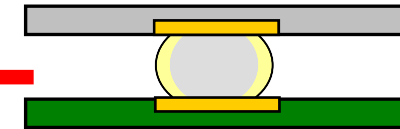
Nanosolder must be patternable like existing pastes



Paste should melt near or below the Sn/Pb eutectic point

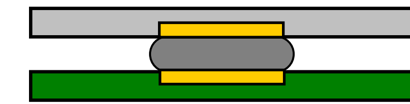






The nanoparticles must remain molten and coalesce fully (aided by flux)

The molten solder must wet the joint (aided by flux)



The joint then needs to re-solidify at near Sn/Pb processing temperatures

Following solidification the solder should behave thermally and mechanically like the bulk alloy, and re-melt at the higher bulk alloy melting temperature.

Legend

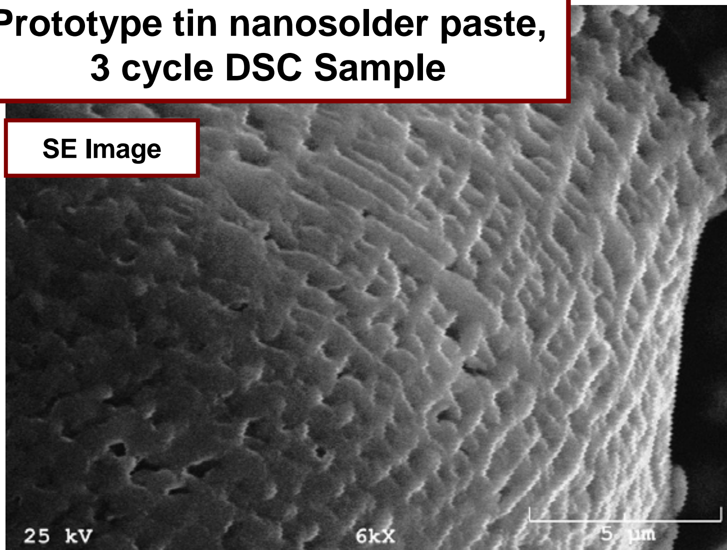
Why is this Important?

- NanoSolders are powerful new tools to allow us to lower assembly temperatures
  - To prevent damage to components and boards
  - To allow us to assemble next generation products with process temperature constraints as low as 125°C
- The iNEMI program is developing a model system
  - To characterize joint metallurgy and properties
  - To explore process compatibility and reliability

Evidence of Nanoparticle Coalescence

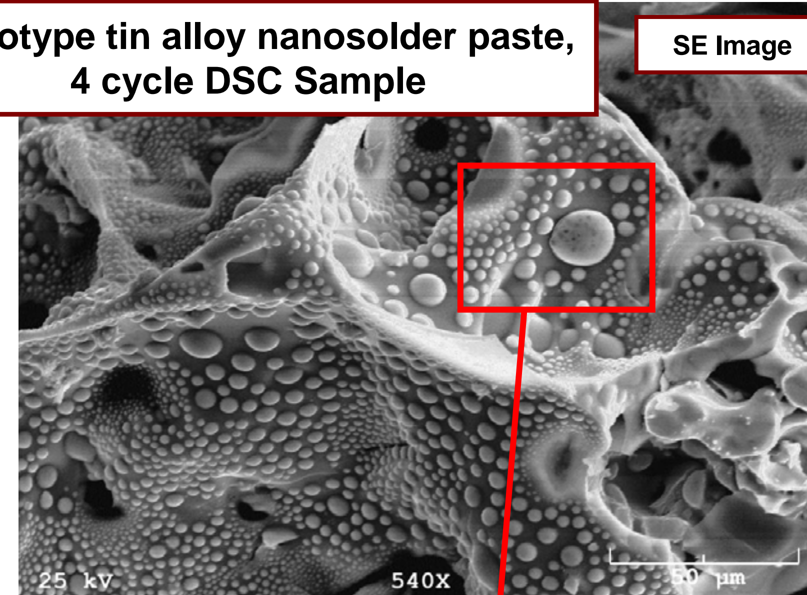
Prototype tin nanosolder paste, 3 cycle DSC Sample

SE Image



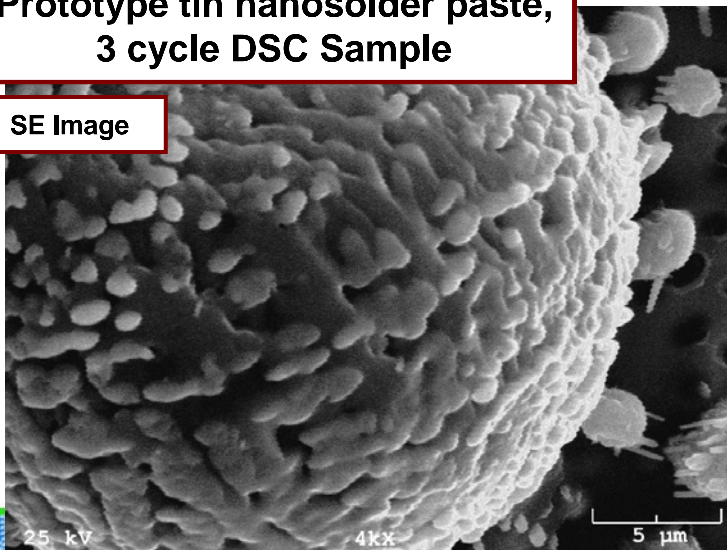
Prototype tin alloy nanosolder paste, 4 cycle DSC Sample

SE Image

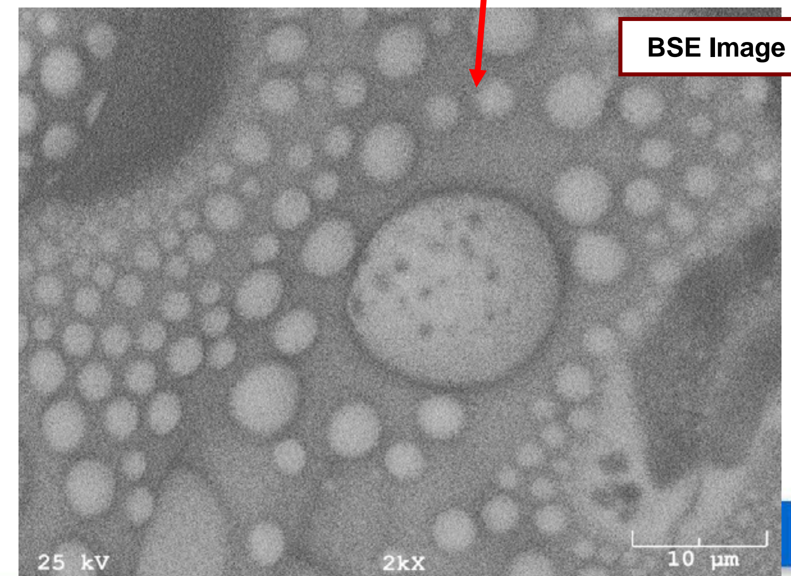


Prototype tin nanosolder paste, 3 cycle DSC Sample

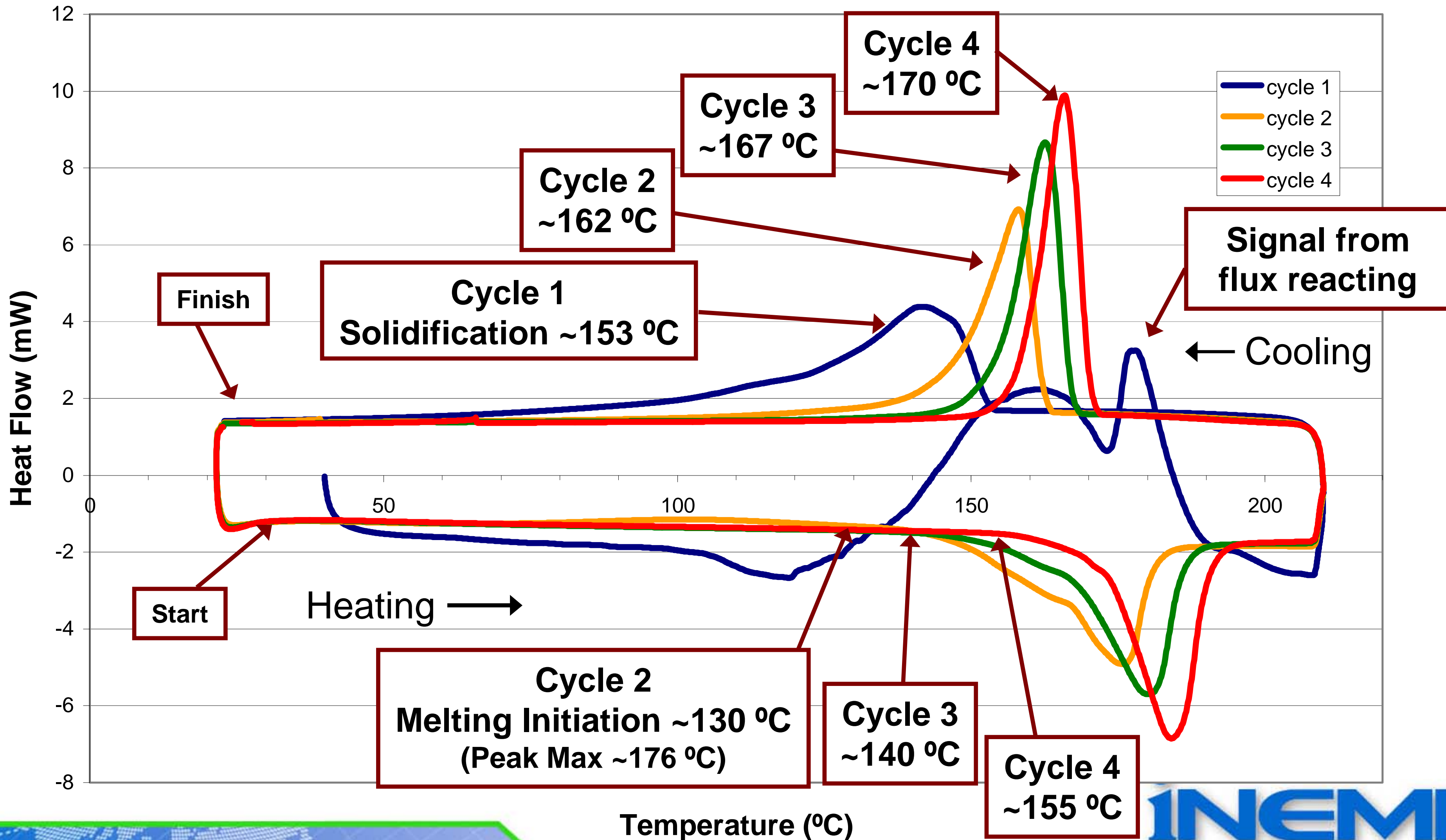
SE Image



BSE Image



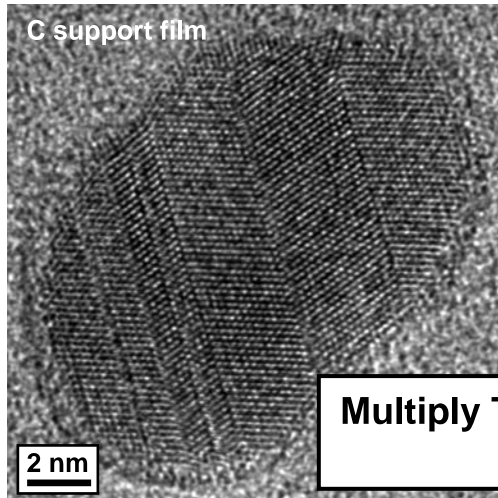
DSC Examination of Coalescence in a Prototype Tin Nanosolder Paste



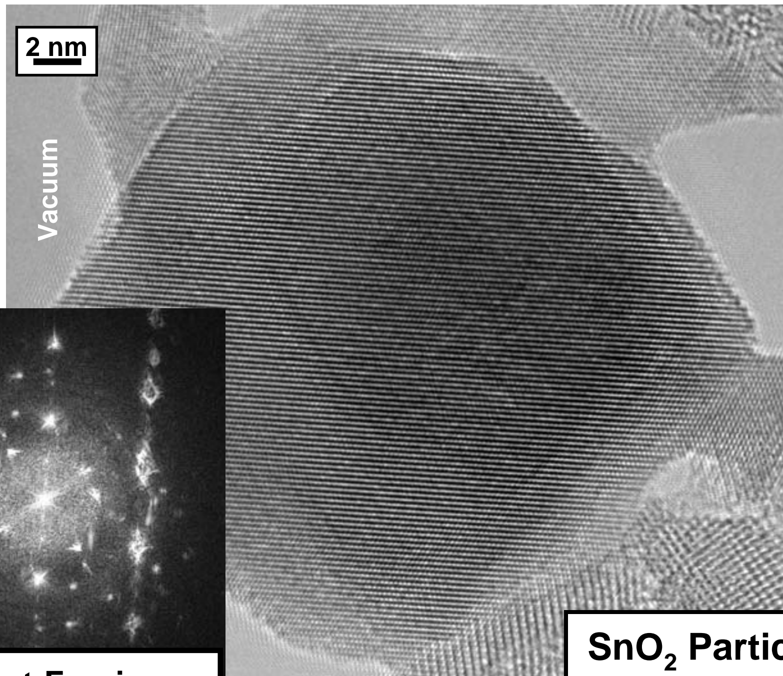
High Resolution Characterization

Nanoparticles are very reactive and oxidize readily after short exposure times if unprotected.

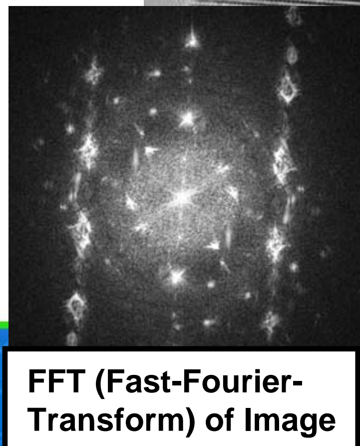
Nanoparticles shown here are tin oxide, but may have been metallic before they were exposed to air during sample preparation.



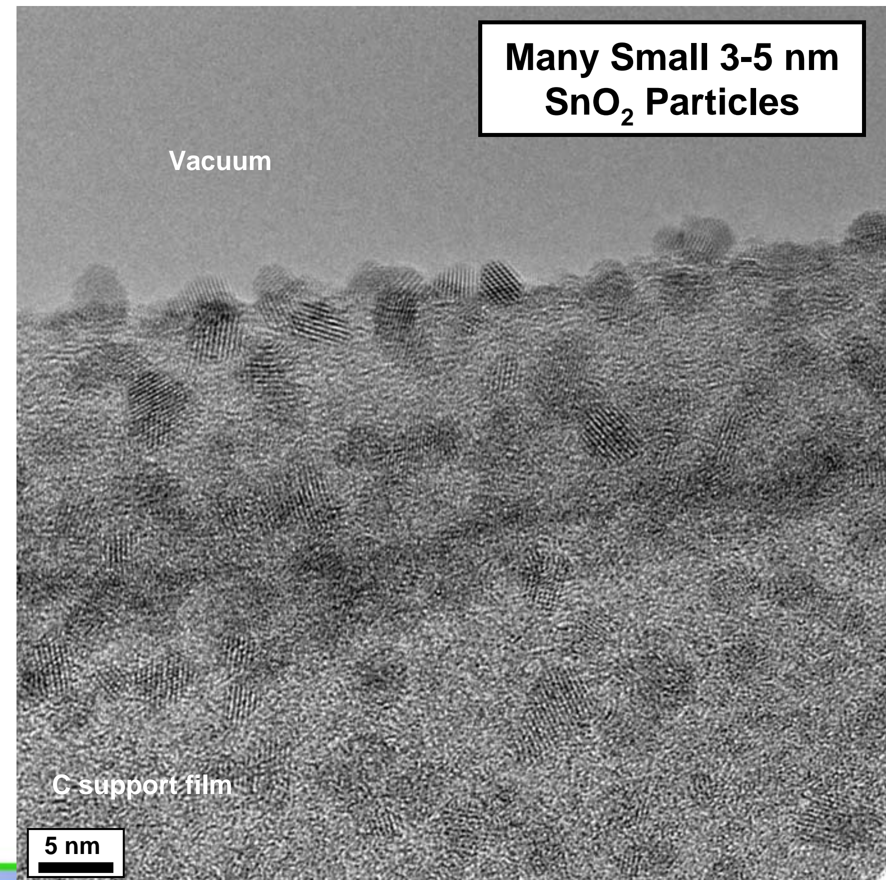
Multiply Twinned Sn Oxide Particle



SnO_2 Particle



FFT (Fast-Fourier-Transform) of Image



Many Small 3-5 nm SnO_2 Particles

Other Groups Also Working on Nanosolder

- **Tin and tin alloy nanoparticles have been chemically produced by several groups**

C Nayral, et al., Chem. Eur. J., 6, No. 22 (2000) ➔ Synthesis of Sn nanoparticles

H Jiang, et al., Chemical Physics Letters, 249, 492 (2006) ➔ Synthesis, characterization, and DSC of Sn nanoparticles

LY Hsaio and JG Duh, J., Electrochem. Soc., 152, J105 (2005) ➔ Synthesis and DSC of Sn/Ag/Cu nanoparticles

H Jiang, et al., Chem. Mater., 19 (18), 4482 (2007) ➔ Synthesis, characterization, and DSC of Sn/Ag nanoparticles

Melting point suppression has been observed in some cases.

Current Progress and Technical Approach

- **MetaMateria Partners has manufactured prototype nanosolder pastes**
  - Tin or tin alloy nanoparticles fabricated by Metamatera Partners
  - Flux provided by the Indium Corporation of America
  - Melting point and coalescence behavior characterized by Purdue University

- **Significant melting point depression observed**
  - Tin and SAC alloy nano particles with flux have been thermally characterized by differential scanning calorimetry (DSC) and shown to melt at temperatures far below 183 ^{0}C.

- **Partial coalescence has been seen in the prototype nanosolder pastes**
  - High resolution characterization of nanoparticle structure and of particle melting and coalescence behavior has been conducted by transmission electron microscopy (TEM) in an FEI Titan 80/300 TEM with a hot-stage environmental cell at Purdue University.

Current papers/presentations from iNEMI NanoSolder Team Members

- Gordon Research Conference Poster, August 2006, **“Examination of Tin Nanoparticle Melting and Coalescence,”** Kevin Grossklaus, Carol Handwerker, Eric Stach, Purdue University
- Materials Research Society, December 2006, “**Examination of the Melting Point of Sn Nano-Particles for Nanosolder Applications**” Kevin Grossklaus, Carol Handwerker, Eric Stach, Purdue University
- PAN-PAC 2007, January 2007, **"Warm Manufacturing,"** Alan Rae, NanoDynamics Inc., Marc Chason, and Andrew Skipor, Motorola Inc.
- Materials Research Society, March 2007, **“Thermal and TEM analysis of Sn Nano-Particles for Use in Nanosolder Applications,”** Kevin Grossklaus, Eric Stach and Carol Handwerker, Purdue University
- Semicon West, July 2007, **“Nanotechnology and Printed Electronics,”** Alan Rae
- Purdue Master’s Thesis, August 2007, **“Melting and Coalescence Behavior of Tin Nanoparticles for Use in Low Temperature Solder Applications,”** Kevin Grossklaus
- MS&T 2007, September 2007, **“Development of Pb-Free Nanoparticle Solders for Microelectronic Packaging,”** Kevin A. Grossklaus, Carol A. Handwerker, Eric A. Stach, Purdue University, R. Rao Revur, Suvankar Sengupta, MetaMateria Partners, and Hong-Sik Hwang, Indium Corp.
- SMTAI, October 2007, “**NanoSolder and Fusible Metals for Die Attach and Interconnection,** “Alan Rae, NanoDynamics Inc.

iNEMI

Summary

•DSC testing has shown prototype nanosolder paste melting temperatures consistently below 190 ^{0}C and in some cases partial melting below 150 ^{0}C can be achieved.

•Partial coalescence of particles can be inferred from DSC testing and was directly seen by in-situ TEM experimentation.

•It is possible that coalescence is limited due to low metallic particle concentrations and interference from flux and other materials in the prototype nanosolder pastes. Increasing the particle concentration of the pastes should improve coalescence.

•Additional in-situ TEM work will be needed to clarify the specifics of melting in this system. This will allow a more detailed interpretation of the behavior seen in the DSC.

Work is ongoing by the iNEMI Project Team.

New prototype materials are being examined by DSC and other characterization techniques.
New macroscale melting experiments are being conducted as a first step towards joint creation.

Pb-Free Nanosolder Project

Work is ongoing by the iNEMI Project Team.

New prototype materials are being examined by DSC and other characterization techniques.

New macroscale melting experiments are being conducted as a first step towards joint creation.

MetaMateria Partners and Purdue University gratefully acknowledge the support of NSF through the grant:

STTR (Small Business Technology Transfer) Phase I - Low Temperature, Lead-Free Nanosolder for Microelectronics

Email contacts:

Jim McElroy

jmcelroy@inemi.org

Bob Pfahl

bob.pfahl@inemi.org