Development of Nano Lead Free Solders –Challenges and Future Research Topics

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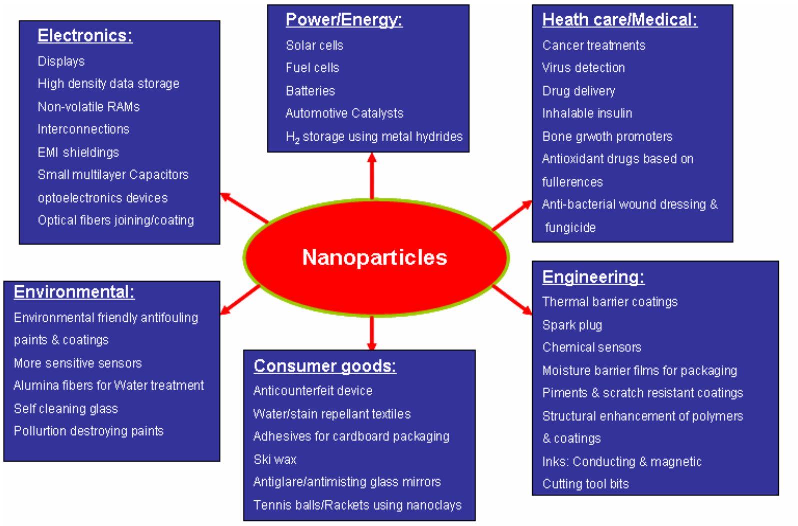
Definition of Nano Particles

Particles in size range 10^{-9}m are knwon as nanoparticles or sub-micron particles. They are also known as quantum dots due to quantum property possess by them.

Nanoparticles in Various Fields



Nanoparticles

Electronics:
- Displays
- High density data storage
- Non-volatile RAMs
- Interconnections
- EMI shieldings
- Small multilayer Capacitors
- optoelectronics devices
- Optical fibers joining/coating

Power/Energy:
- Solar cells
- Fuel cells
- Batteries
- Automotive Catalysts
- H_2 storage using metal hydrides

Heath care/Medical:
- Cancer treatments
- Virus detection
- Drug delivery
- Inhalable insulin
- Bone grwoth promoters
- Antioxidant drugs based on fullerences
- Anti-bacterial wound dressing & fungicide

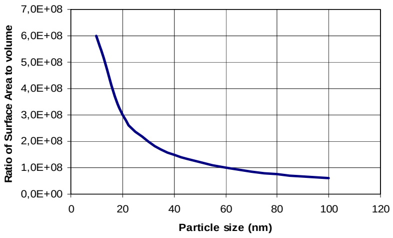
Environmental:
- Environmental friendly antifouling paints & coatings
- More sensitive sensors
- Alumina fibers for Water treatment
- Self cleaning glass
- Pollurtion destroying paints

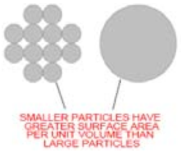
Consumer goods:
- Anticounterfeit device
- Water/stain repellant textiles
- Adhesives for cardboard packaging
- Ski wax
- Antiglare/antimisting glass mirrors
- Tennis balls/Rackets using nanoclays

Engineering:
- Thermal barrier coatings
- Spark plug
- Chemical sensors
- Moisture barrier films for packaging
- Piments & scratch resistant coatings
- Structural enhancement of polymers & coatings
- Inks: Conducting & magnetic
- Cutting tool bits

Motivation for Development of Nano Lead Free Solders

- **Unique properties of materials in nano-scale**
  - Large surface area per unit volume
  - Large surface energy
  - Low melting point (difference can be as large as 100ºC)
- **Depression in melting temperature**
  - Reduce processing temperature
  - Reduce thermal stresses during processing
- **Increased strength of solder alloys**
  - Finer microstructure
  - Less prone to grain coarsening
  - Restriction of dislocation movement and grain boundary sliding
- **Interconnection miniaturization**
  - Very small pitch applications
  - Increase fine pitch interconnection reliability





Approach in Nano Lead Free Soldering

- Nano-size effect: Lower melting point leads to lower reflow temperature
- Grain size control: Bimodal distributed solder system (nano-sized powder mixed together with micro-sized particle technology in solder may improve mechanical properties of the solder joint)

Current Related Research Worldwide on Nano Lead Free Solders

- **iNEMI Lead-Free Nano-Solder Project, USA**
  - Application of Nanotechnology to Suppress Non-Lead Solder Reflow Temperature (Aerodynamics, USA)

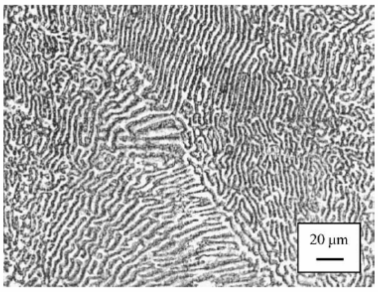
- Synthesis and Application of Novel Lead-Free Solders Derived from Sn-based Nanopowders by L. Y. Hsiao, J. G. Duh, “Synthesis and Characterization of the Lead-Free Solders with Sn-3.5Ag-xCu Alloy Nanoparticles by Chemical Reduction Method,” *Journal of The Electrochemical Society*, Vol.152, No.9 (2005), pp.J105-J109.

Experimental Approach

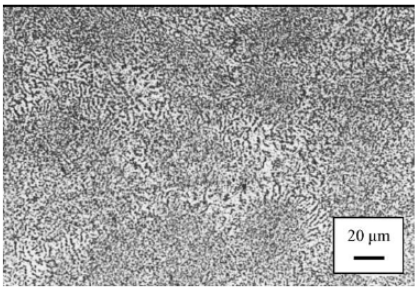
- **Elements:**
  - Cu_6Sn_5 nanopowder, Sn-3.5Ag solder paste (Mechanically Mixing, Ratio: 1.295wt%, Surface finish: ENIG)
- **Nanopowders synthesis method:**
  - Cu_6Sn_5 nanopowders were synthesized by precipitation with sodium borohydride ($NaBH_4$) in aqueous solutions at room temperature.
  - Appropriate amounts of $SnSO_4$, $AgNO_3$, and $Cu(NO_3)_2 \cdot 2.5H_2O$ were dissolved in aqueous solutions as the precursors for Cu_6Sn_5 nanopowders.
- **Intermetallic Compounds (IMCs)**
  - Needle-type $(Ni,Cu)_3Sn_4$ and Hexagonal $(Cu,Ni)_6Sn_5$
- **Shear Test Result**
  - The ball shear strength of Cu_6Sn_5-contained joint was shigher than that of the bare SnAgCu one owing to the nano Cu_6Sn_5 reinforcement. However, after more than five reflows, the effect is lost and brittle failure mode controls the ball shear strengh.

Effect of nanoparticles to control the grain size

“Influence of titanium dioxide nanopowder addition on microstructural development and hardness of tin–lead solder”, D.C. Lina, G.X. Wanga, T.S. Srivatsana, Meslet Al-Hajria, M. Petrarolib, Materials Letters 57 (2003) 3193– 3198.



Conventional eutectic Sn-37Pb



Sn-37Pb with 0.5Wt% titanium dioxide nano-powder

Effect of nanoparticles to control the IMC layer thickness (ECTC 2006)

A Study of Nano Particles in SnAg-Based Lead Free Solders for Intermetallic Compounds and Drop Test Performance

Masazumi Amagai, Modeling and Characterization,
Ysukuba Technology Center, Texas Instruments, Japan

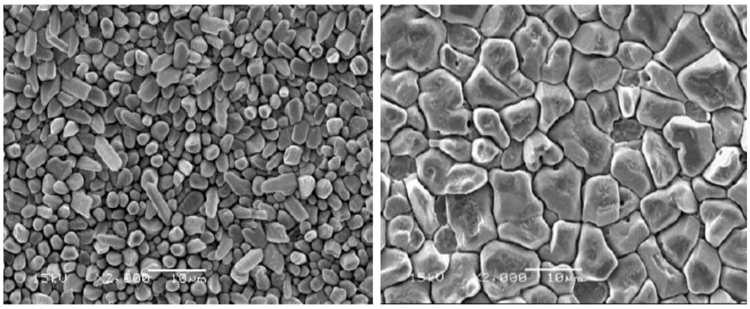
Experimental Approach

Elements: Co, Ni, Pt, Al, P, Cu, Zn, Ge, Ag, In, Sb, Au nano particles Sn-3.0Ag (Multiple reflow 245^0C, Pull), Sn-1.0Ag solder paste (Drop)

Multiple reflow result: Co, Ni and Pt were solved in IMC, which does not increase IMC grain size and thickness significantly after 4 time solder reflow processes.

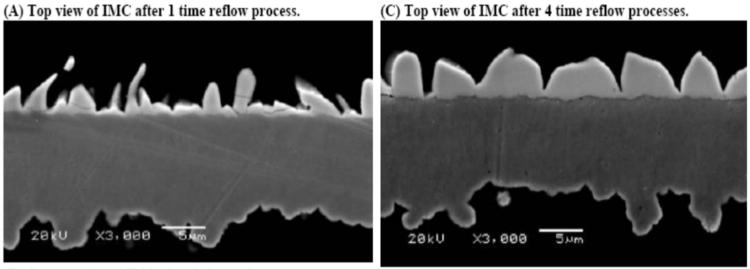
Pull test result: Co, Ni or Pt including in Sn-3.0Ag-based lead free solders show low frequency of occurrence of IMC fracture.

Drop test result: Ni, Co and Pt were very effective to increase the drop test performance.



(A) Top view of IMC after 1 time reflow process.

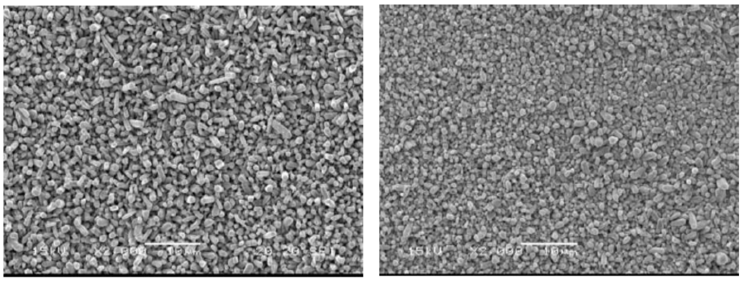
(C) Top view of IMC after 4 time reflow processes.



(B) Cross section of IMC after 1 time reflow process.

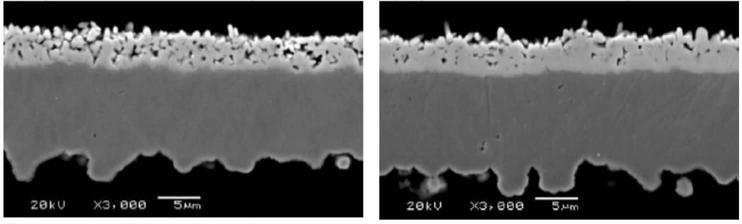
(D) Cross section of IMC after 4 time reflow processes.

Intermetallic Compounds with Sn-3.0Ag



(A) Top view of IMC after 1 time reflow process.

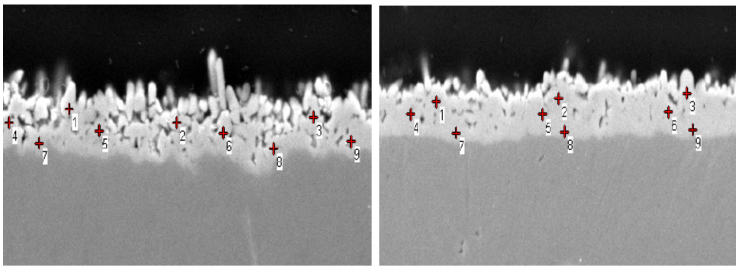
(C) Top view of IMC after 4 time reflow processes.



(B) Cross section of IMC after 1 time reflow process.

(D) Cross section of IMC after 4 time reflow processes.

Intermetallic Compounds with Sn-3.0Ag-0.03Co



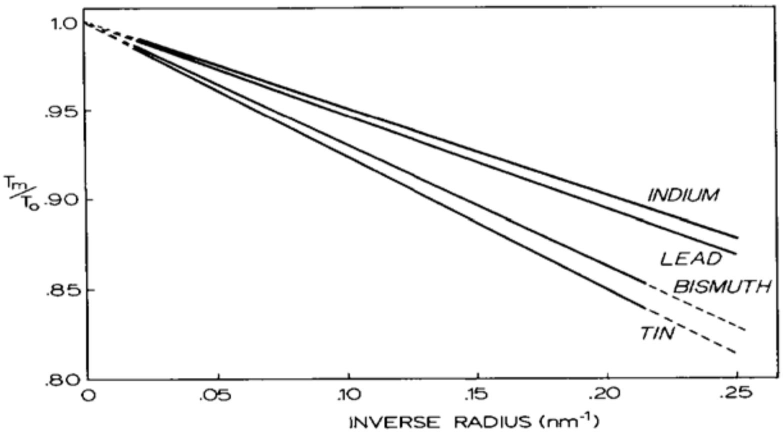
Location	Co	Cu	Sn	Total
1 (111,137)	------	45.08	54.92	100.00
2 (254,150)	3.29	44.21	52.50	100.00
3 (436,145)	1.87	43.74	54.39	100.00
4 (31,150)	2.14	44.93	52.92	100.00
5 (151,158)	2.53	45.20	52.28	100.00
6 (316,160)	2.43	46.91	50.67	100.00
7 (71,170)	2.08	48.22	49.71	100.00
8 (383,175)	2.06	48.21	49.74	100.00
9 (486,168)	1.77	45.51	52.71	100.00

(A) IMC element analysis after 1 time reflow process.

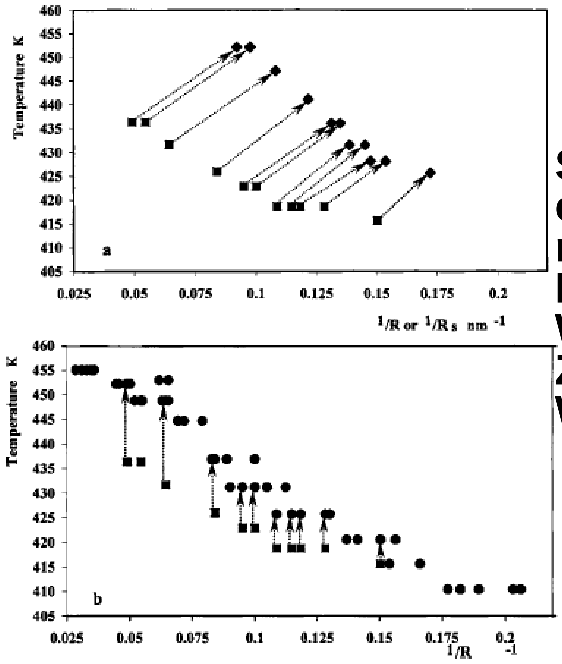
Location	Co	Cu	Sn	Total
1 (101,130)	2.11	42.75	55.14	100.00
2 (268,127)	1.99	44.53	53.48	100.00
3 (443,122)	2.38	43.58	54.03	100.00
4 (66,142)	2.65	45.01	52.34	100.00
5 (246,142)	1.42	45.88	52.71	100.00
6 (418,140)	2.02	44.82	53.16	100.00
7 (128,160)	0.88	48.13	50.99	100.00
8 (276,159)	0.50	47.99	51.51	100.00
9 (451,157)	1.66	45.36	52.99	100.00

(B) IMC element analysis after 4 time reflow processes.

Reduced temperature as reciprocal particle size of In, Pb, Bi and Sn (Allen et al, *Thin Solid Films, 144* (1986) 297-308)



PHYSICAL REVIEW B 69, 144121 (2004)



Solid-liquid equilibria in nanoparticles of Pb-Bi alloys by W. A. Jesser, R. Z. Shneck and W. W. Gile

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Nanoparticles production

Top down Approch

- Mechanical Milling
- Lithography (hybrid technology)
- Electro-explosion (thermal / chemical)
- Laser Abilation (Thermal)
- Spark Erosion (Electric Arc Disharge)

Bottom up Approch

- Sol-gel technique
- Aerosol based process
- Chemical vapour deposition (CVD)
- Molecular condensation
- Electrospinning
- Self Assembly

Nano-sized Pb free Alloys manufactured

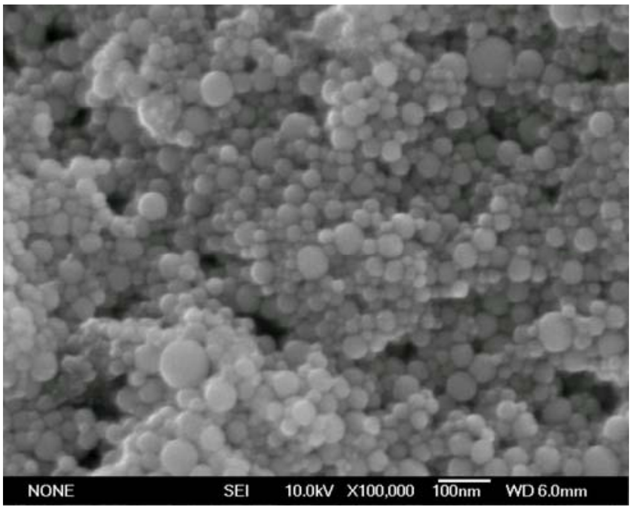
1.Sn3,0Ag0,5Cu - 219 °C

2. Sn4,0Ag0,5Cu - 217 °C

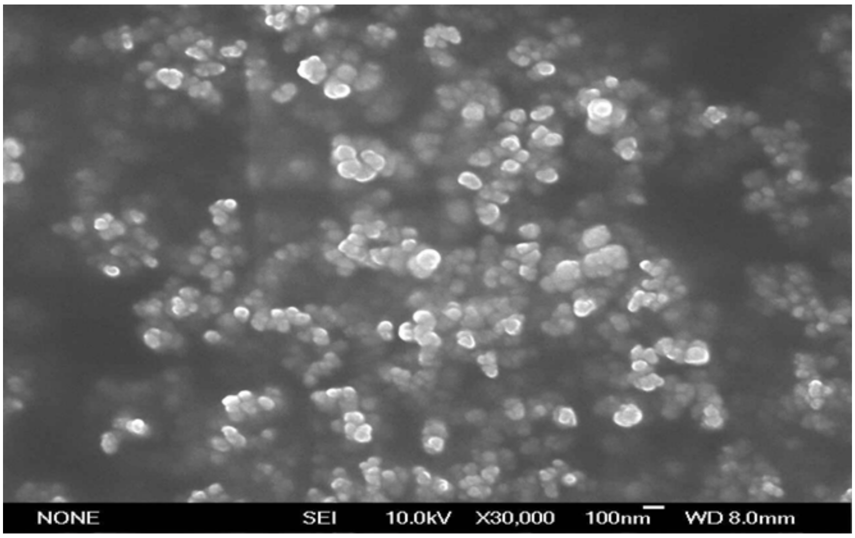
3.Sn0,4Co0.7Cu - 224°C

4.Sn57Bi - 139 °C

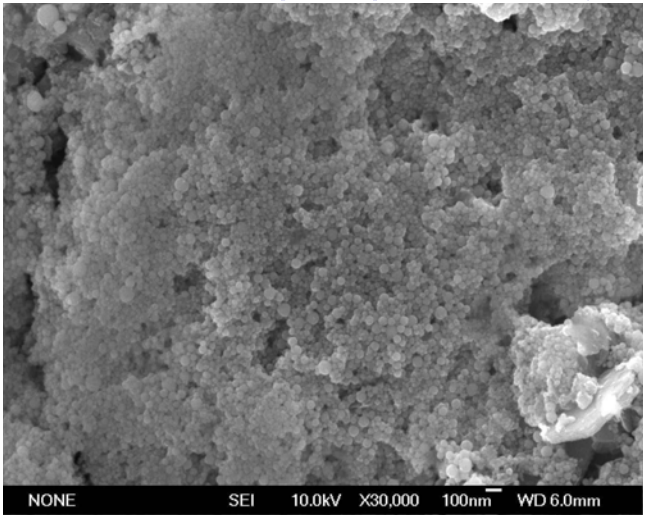
Sn3,0Ag0,5Cu nanoparticles



Sn0,4Co0,7Cu nanoparticles

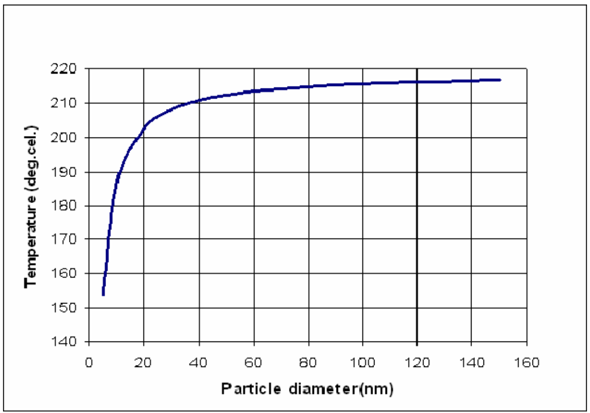


High volume of nanoparticles produced with good size control and distribution (Example: SAC305 system)



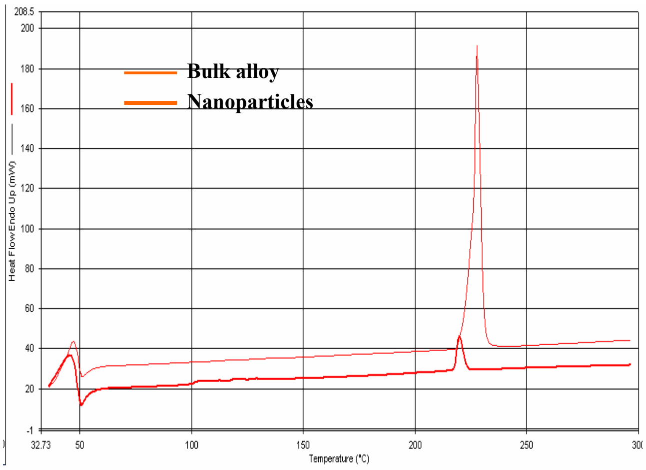
Melting Point Depression

$$\Delta T = T_m^{bulk} - T_m(r) = \frac{2T_m^{bulk}}{H_m^{bulk}\rho_s r}\left[\sigma_s - \sigma_L\left(\frac{\rho_s}{\rho_L}\right)^{\frac{2}{3}}\right]$$



Sn4,0Ag0,5Cu Nano alloy particles

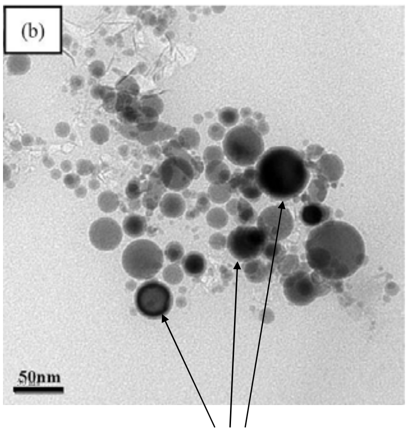
DSC Ananlysis



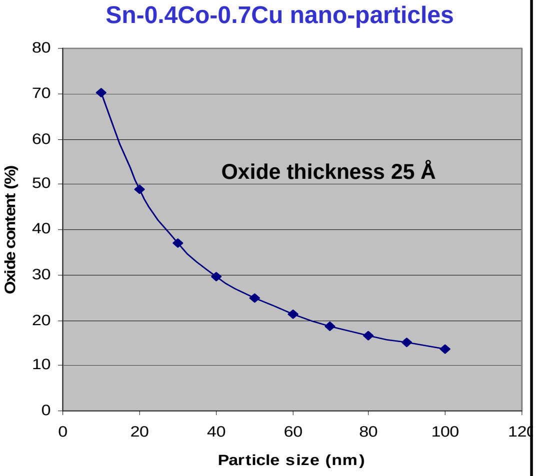
Onset calculation showed about 3°C depression in melting point.

Sn4,0Ag0,5Cu

Oxide content in nano-particles



Oxide layer



Details of Reflow Oven with N2 Gas

Purity of Nitrogen gas used – 99.996% at 1 second pulse rate.

Solder paste formulation

Composition:

1. Lead free Alloy Nanoparticles - ~ 50 wt%
   in paraffin oil
2. Flux - ~ 50 wt%

Component mounting

Components used:

1. 1812 Capacitors with tin metallization on end (big).
2. 1206 Capacitors with tin metallization on end (small).

Test Board:

1. Ceramic test board

Reflow conditions:

1. Reflow temperature - 290ºC (for 2 Minutes)
2. Atmosphere - Nitrogen (Inert)

Component Mounting Test

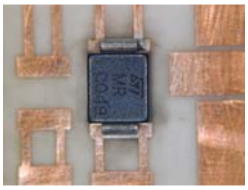
Sn0.4Co0.7Cu Nanoparticles with active

Big Components, 1812

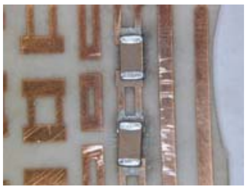
Small Component, 1206

Contact Resistance by four probe - 0.2 mΩ in all cases.

Sn4.0Ag0.5Cu Nanoparticles with active



Big Component, 1812



Small Components, 1206

Future Research Topics

- **Aim: Develop prototype nanosolder lead free paste in 3-5 years time**
- **Issues:**
  - **Single particle melting point measurement techniques**
  - **Flux formulation and characterisation**
  - **Paste Characterisation**
  - **Application Technology including stencil printing, dispensing and jetting**
  - **Reliability characterisation and testing**

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