Functionalisation of Copper Nanoparticles to Enable Metallisation in Electronics Manufacturing

Dr David Hutt, Dr Mark Sugden
Loughborough University
Email D.A.Hutt@lboro.ac.uk

Dr Andy Cobléy, Dr John Graves
Coventry University
Email A.C.Coble@coventry.ac.uk
Project Overview

- Project funded by the IeMRC
- Commenced March 2012
- 24 person months of effort at both universities
- Several industrial partners
Outline

- Background
- Project Approach
- Particle Surface Modification
- Particle Dispersion
- Initial Results
- Coating of Substrates
- Conclusions
Electroless Copper

- Chemical plating technique to deposit copper without the need for electrical contact
  - Ideal for insulating substrates
- Reducing agent in the solution reduces \( \text{Cu}^{2+} \) ions to \( \text{Cu} \) metal on a suitable surface
Applications of Electroless Copper

- Ideal for electrically insulating substrates
  - e.g. Glass, LTCC, Plastics

- Widespread use within the Printed Circuit Board (PCB) industry for the metallisation of vias

Printed Circuit Board (PCB) Metallisation

- Drilled PCB
- Sn / Pd Colloid
- Electroless Cu
- Metallised via
Catalysts for Electroless Plating

- Insulating substrates usually require activation before electroless plating can commence
  - Catalyst is deposited from a chemical bath
  - Sn/Pd colloid (Pd nanoparticles) is typically used
    - Provides Pd metal sites at which Cu can nucleate
    - Expensive, limited adhesion to some substrates (e.g. glass), many substrates require pre-treatment

Sn⁴⁺ shell

Electroless Cu
**Proposed Process**

- **Aim to replace the Sn/Pd catalyst with a less expensive Cu catalyst**
- **Using commercially available Cu nanoparticles (CuNPs)**
- **Copper nanoparticles functionalised (coated)**
  - Improve stability, dispersion and adhesion
  - Aim to remove the need for substrate pre-treatment
- **Suspended in a solvent and adsorbed onto substrates**

![Diagram showing the process]

1. **Bare CuNPs**
2. **Coat**
3. **Dispersions of functionalised CuNPs**
4. **Immerse substrate to attach CuNPs**
5. **Electroless copper deposition**
Previous Work

Unfunctionalised Cu nanoparticles dispersed, drop coated on FR-4, dried and plated.

Standard Pd based process

Through hole plating of printed circuit boards using ultrasonically dispersed copper nanoparticles, A.J. Cobley et al., Circuit World 36(3) 9-13 (2010)
Monolayer Organic Coatings

- Thin organic films formed by the adsorption of organic molecules onto surfaces
  - Typically formed by adsorption from solution
- Head group (Y) attaches to the substrate surface
- Tail groups (X) exposed creating a “new” surface
- Densely packed single layer of molecules

\[ \text{Self-assembled monolayer} \]

2-3 nm
Functionalised Nanoparticles

- Organic coatings can be applied to nanoparticle surfaces
  - Reduce the rate of oxidation
  - Improve dispersion stability
  - Exposed functional groups can enhance adhesion to the substrate
Stability of Functionalised Particles

- **Functionalised CuNPs in solvent**
- **Bare CuNPs in solvent with glacial acetic acid added**
- **Functionalised CuNPs in solvent with glacial acetic acid added**
Particle Dispersion

- Dynamic Light Scattering (DLS) used to measure particle dispersion
  - Malvern Instruments Zetasizer
- Different ultrasound systems investigated for dispersion
- Aim to achieve good dispersion to enhance attachment
- Primary particle size of commercial powder of 25 nm

TEM unfunctionalised particles

TEM functionalised particles
Output from DLS

Sn / Pd Colloid
Z-Average 10.56 nm
PdI 0.284

Dispersed Cu Nanopowder
Z-Average 233.3 nm
PdI 0.342

Z-Average 160.2 nm
PdI 0.219
Effect of Ultrasound on Dispersion

Mean Diameters of CuNPs (25nm primary particle size) as a function of ultrasonic processing time and power, 20 kHz, 0.01% wt.vol.
Particle Dispersion

Size Distribution by Number

Initial distribution

After ultrasonic agitation

Number (%)

Size (d.nm)

0.1 1 10 100 1000 10000

0 5 10 15

Record 38: 160113-1 Average
Record 45: 160113-8 Average

Primary particle size 25 nm
Secondary aggregates
Large aggregates in initial material
Initial Plating Trials – Drop Coating

- Functionalised Copper nanoparticles shown to activate the electroless plating process
  - Particle solution dropped onto substrate and dried
  - Peel tests suggest good adhesion

FR4 samples as plated

FR4 samples after tape peel test

16
FR4 Dip Coating

- FR4 immersed in CuNP dispersion for 10 minutes
- SEM images show good coverage of particles
- Roughened and smooth FR4 under investigation
FR4 Plated Samples

- Dip coated samples plated with electroless copper for 10 minutes
FR4 Plated Samples

- Good coverage of the substrate was achieved
- Rough surface enhances adhesion so that peel test is successful

FR4 samples after tape peel test
Other Substrates

- Investigating glass, BOPP, PEN, polyimide and ABS substrates
- Substrates can be activated
  - Inconsistent results at this stage
  - Adhesion problematic, especially on smooth surfaces
  - Very dependent on plating and coating parameters

Nanoparticles on glass

Coated ABS samples after tape peel tests
Conclusion

- Project using functionalised copper nanoparticles as catalysts for electroless copper deposition
  - As an alternative to the Sn/Pd catalyst
- Initial results show functionalised particles are able to initiate deposition
- Roughened surface of FR4 activates well and shows good adhesion of electroless copper
- Research is targeting the activation and adhesion of coatings to other substrate surfaces
Acknowledgements

- EPSRC for Financial Support through the Innovative Electronics Manufacturing Research Centre (IeMRC)
- Industrial collaborators:
  - Chestech, Printed Electronics Ltd, Graphic plc, Institute of Circuit Technology

THANK YOU FOR YOUR ATTENTION