Novel inkjettable copper ink utilizing processing temperatures under 100 degrees C without the need of inert atmosphere

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Nanotechnology definition

Nanotechnology comprises all sciences and technologies studying the processes of how two or three molecules bind together until the first aggregate of the same molecules is created achieving the same chemical/physical/biological properties as the bulk material.

How we can work with you

	Process step	Supported by
IP creation	Marketing/production needs	International broad networking
	Technical impasse detected	Talented and dedicated technical/scientific team
	IP research & identification	Powerful IP/scientific/technical data banks and search engines
	IP creation and/or acquisition	Inventive creative research and/or inventions identification
IP protection	IP protection	Dedicated international IP firm
	Partner identification	Strategic partnership
	Proof of concept	Dedicated laboratories and team
IP licensing	IP application/positioning	Licensing agreement
	Technology transfer	Pilot production
	Dedicated new subsidiary	Identified specific large opportunity

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Current research and development activities

Nanotechnology

CNT electron emission	Developing new applications of electron emission from carbon nanotubes.	Electron sources Gas ionization sources Lighting devices
Functionalized Nanomaterials	Enhancing the mechanical and physical properties of materials for improved products.	CNT / nanoclay composites Metalic nano particles CarbAl™ Metal carbon fiber composites
Sensors	Developing sensors, sensor networks and sensor applications for Industrial and Homeland Security needs.	Hydrogen Sono-photonic Ion mobility GMOS™ Enzyme coated CNTs
Nanoelectronics	Developing copper and other technical inks for direct write on flexible substrates.	Technical inks Printable electronics CNT inks and TFTs
Nanoecology	Developing nanotechnology-based improvements for a healthier environment.	PhotoScrub for air cleaning Nanosafety Electro-chromic solid state films

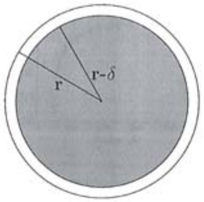
Copper nanoclusters (Cu NC)

- Number of atoms $>$ 10
- Large variety of morphologies
- Surface/volume ratios are very important
- Cu NC are held together by metalic bonds
- Small size Cu NCs ($\sim 10^3$ atoms) show strong size dependency (quantum confinement)
- Cu NCs morphology and size play important role in solid-liquid transitions

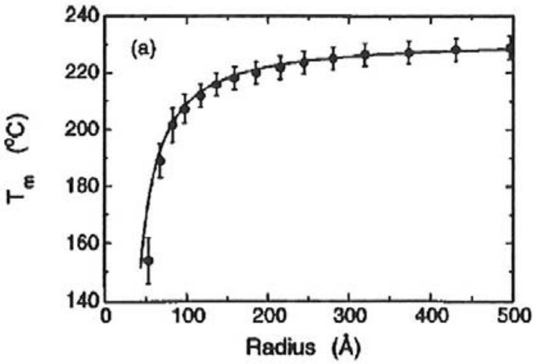
Melting point size dependency

- Generally the melting point shows a monotonic decrease with size
- Utilize the solid core/liquid shell model of melting

$$\mu s\ (p,T) = \mu l\ (p,T)$$



- Example



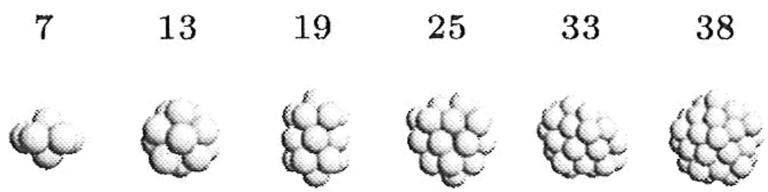
Comparison of theoretical and experimental (solid lines) melting points for tin clusters.

Reference: S. L. Lai, J. Y.Guo, V. Petrova, G. Ramanath, L.H. Allen, Phys. Rev. Lett. 77 (1996) 99.

Copper nanoclusters formation

- The model utilized is adding single Cu atoms to a small initial seed in thermal contact with the cooler surroundings
- Important parameter: rate of temperature change

$$\frac{\partial T}{\partial t} \propto \frac{1}{R}$$



Cu_{38} growth simulation results at T=400°K

Anomalous heat capacity of nanoparticles

- Is the result of a region of coexistence of two or more phases in the melting process
- During the melting and solidification processes single domain clusters or more complex structures with grains may form
- A lot depends on the size and structure of the initial copper nanoparticles

Reference: V. N. Likhachev, G A. Vinogradov, M. I. Alymov, Phys. Lett. A 357 (2006) 236.

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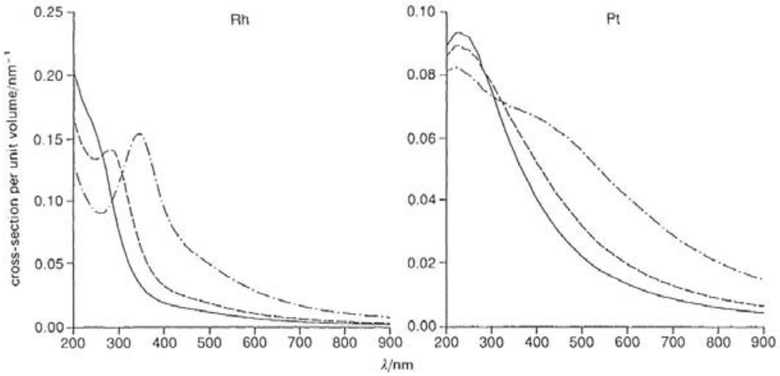
Absorption spectra of nanoparticles

- Absorption spectra of nanoparticles is vastly different than absorption spectra of bulk material
- Absorption spectra depends on size and shape of nanoparticles
- Absorption spectra strongly related to the mean free path of the electrons in the specific material
- Example:



Absorption spectra calculated in the dipole approximation for prolate spheroidal Rh and Pt particles in water. The minor diameter of the particles is 10 nm with different aspect ratios.

Reference: G. Mie, Ann. Phys. 25 (1908) 377.

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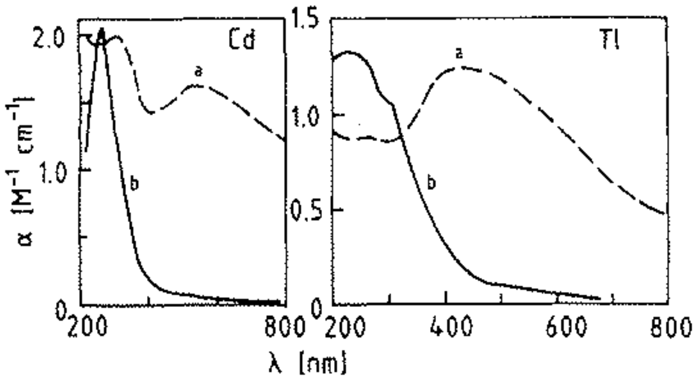
Agglomeration effects

- Example:



Absorption spectra of agglomerated (a) and isolated (b) particles of cadmium and thallium in water.

Reference: A. Henglein, J. Phys. Chem. 97 (1993) 5457

Cu oxide reduction

- We found that proper UV radiation will reduce copper oxides to metalic copper (photosintering).

Targeted ink formulations for photosintering

Based on our understanding of the photosintering mechanism, the following know how was developed in order to achieve optimal copper ink for photosintering:

- Narrow size distribution of copper nanoparticles in dispersion;
- Diameter of nanoparticles in dispersion < 100 nm;
- Suitable passivation during copper nanoparticles production;
- Proper selection between wet and dry processes;
- Suitable choice of vehicles and dispersants;
- Correct choice of loading of copper nanoparticles in dispersion;
- Control agglomeration and achieve proper spectral behavior.

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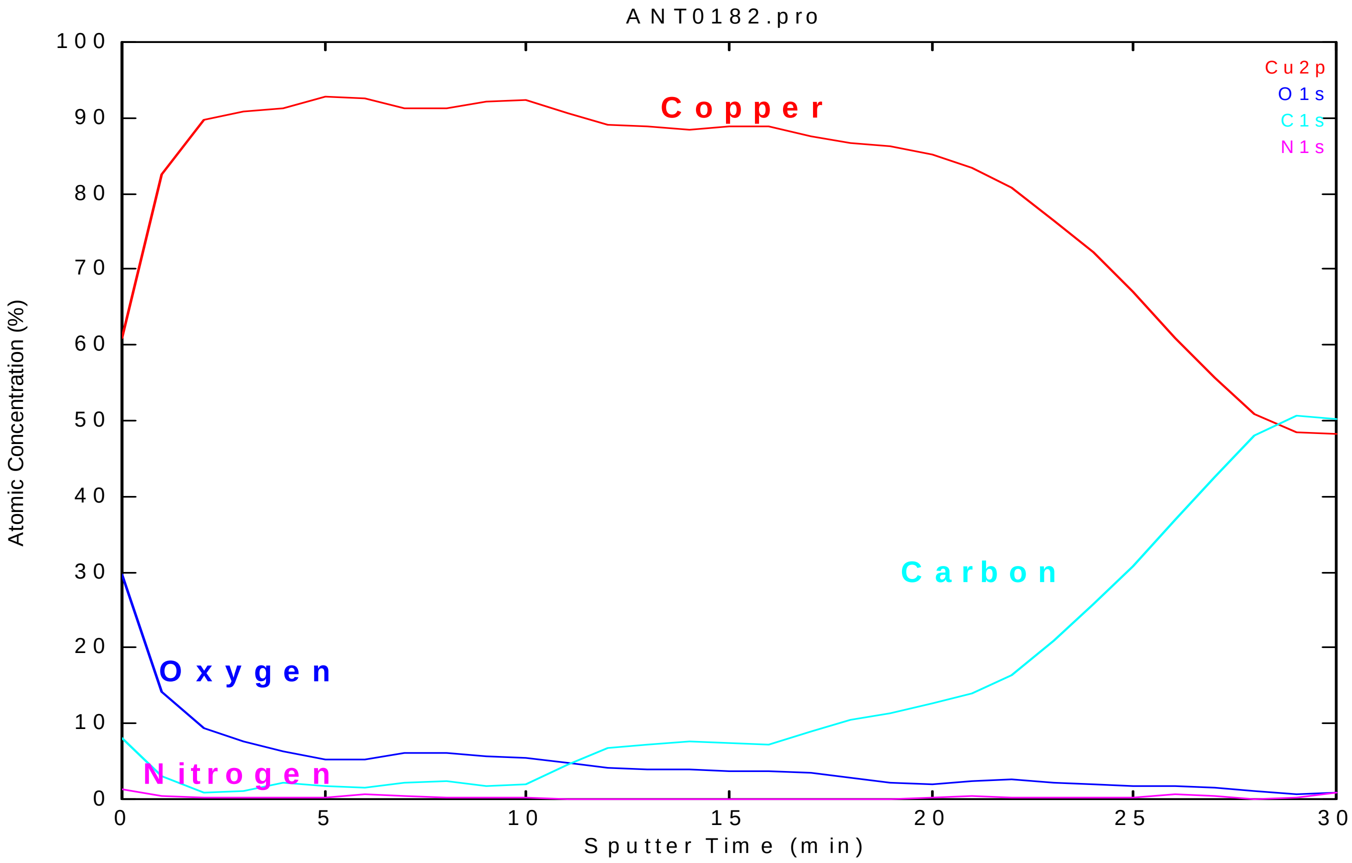
Composition of materials in ink

- Formulations have organic and water-based vehicles and proprietary dispersants
- Vehicles have low toxicities
- Physical properties suitable for inkjetting
- In addition to vehicles and dispersants, other additives are included that control viscosity, surface tension, and surface wetting properties.
- Ink formulations optimized for processing by photosintering
- Copper ink photosintered in air at ambient temperature without need for inert gas
- Copper nanoparticles pretreated for maximum compatibility with the ink components
- Inks stored at ambient temperature in air
- Any oxide not removed by additives will be removed during photosintering

Depth profile of XPS for copper film



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Piezo-inkjet printers

- Dimatix DMP-2800 series printer
- 16 continuously operating nozzles
- Preliminary data obtained
- Lines are 51mm x 225 microns x 0.1 microns

Image of longitudinal patterns-X100

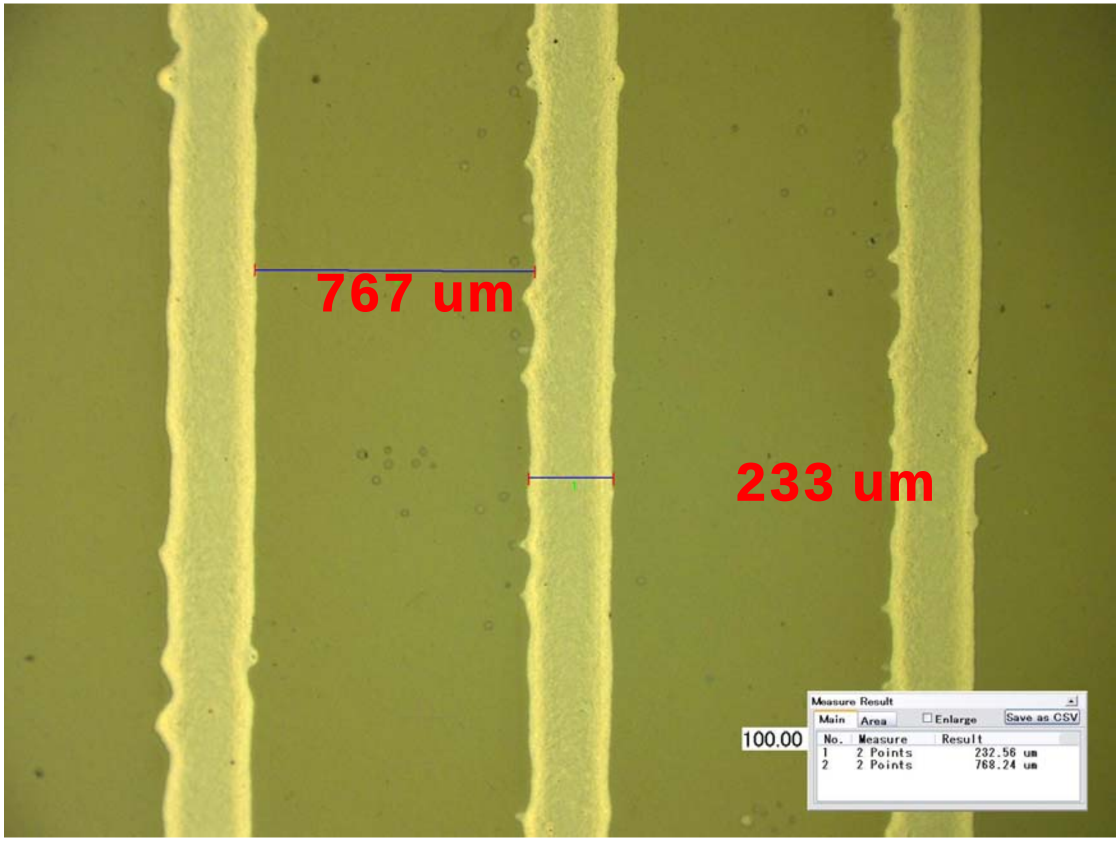

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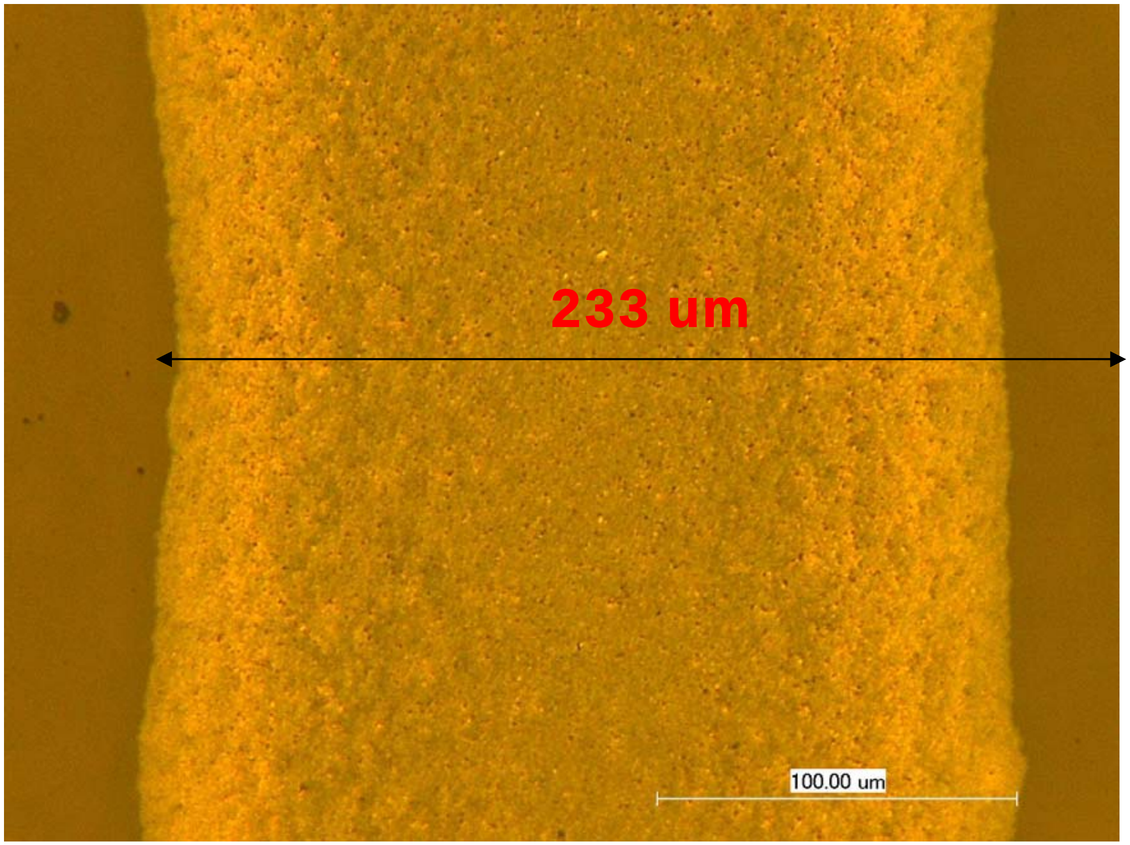
Image of longitudinal patterns- X1000



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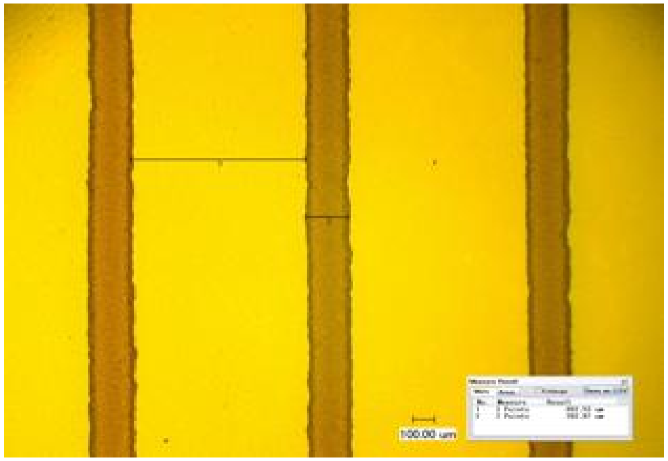
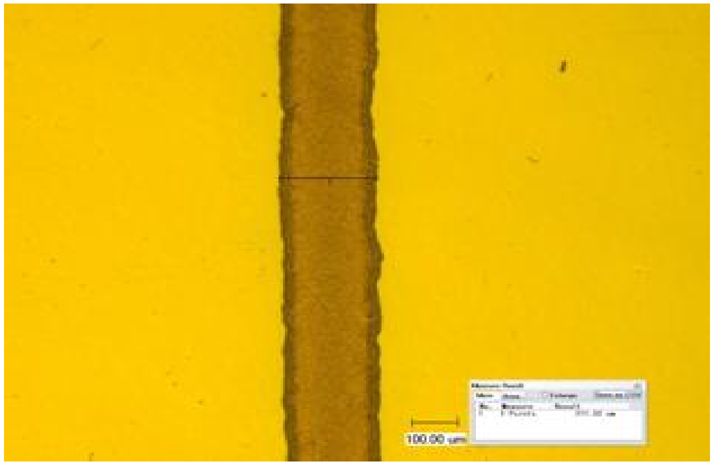
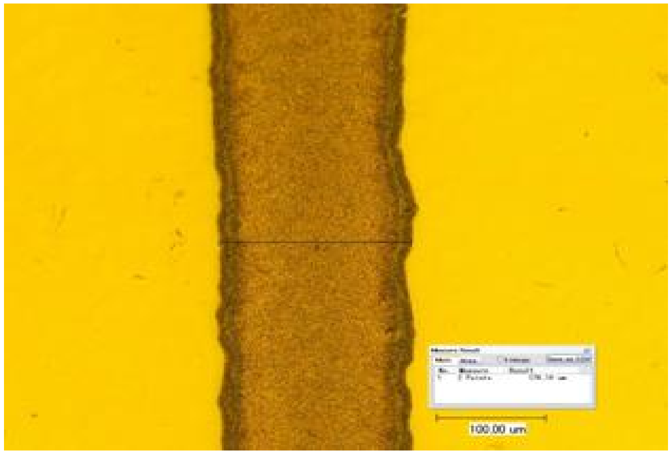
Inkjet line images



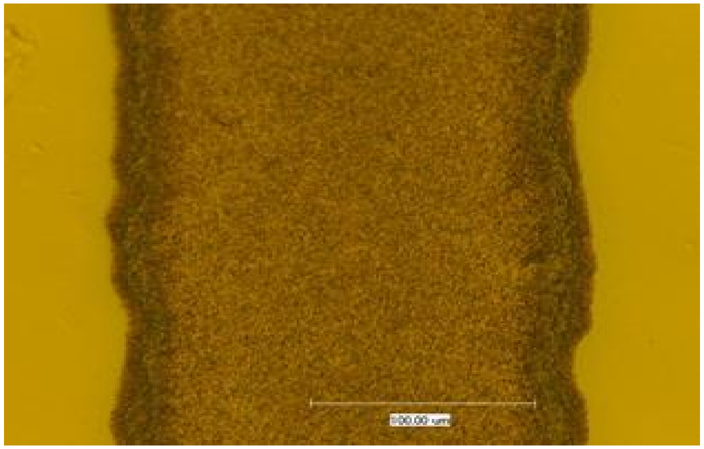
X100



x200



x500



x1000

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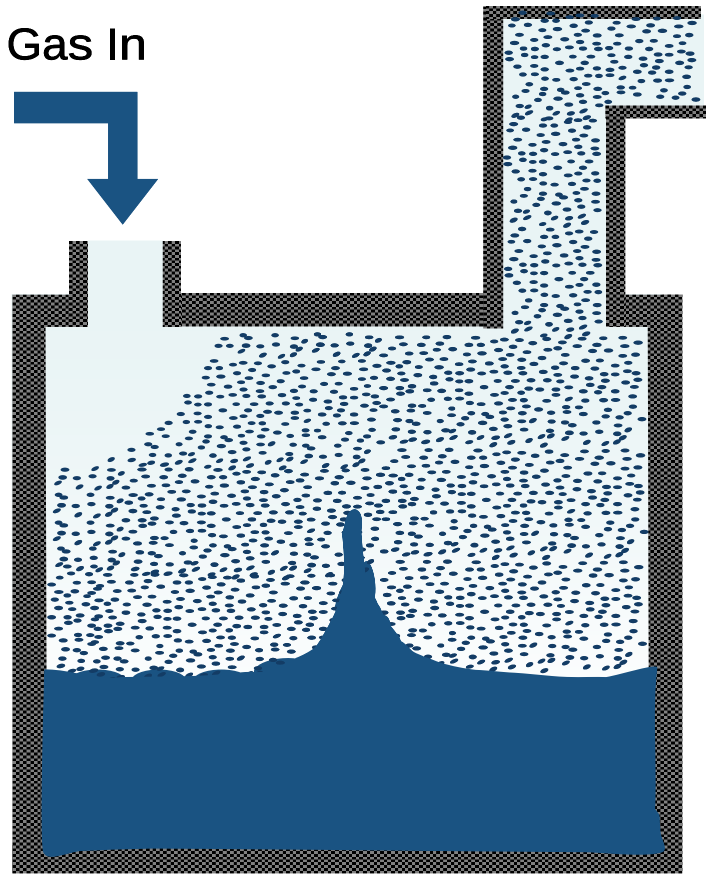
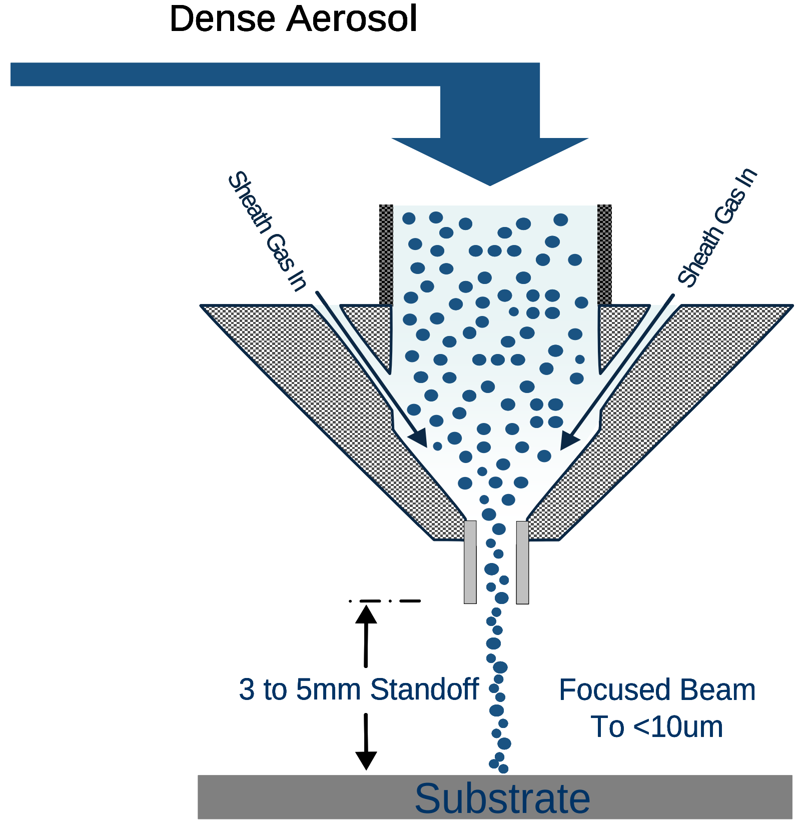
Optomec aerosol inkjet printer





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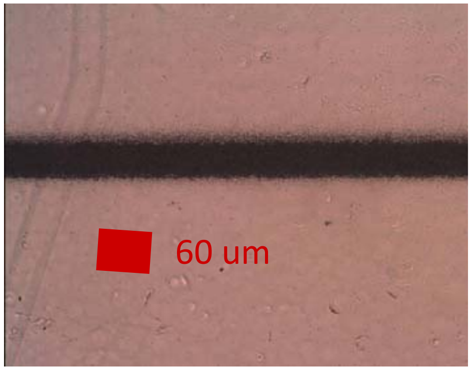
Panoramic view of ANI's printing laboratory

Optomec M^3D features

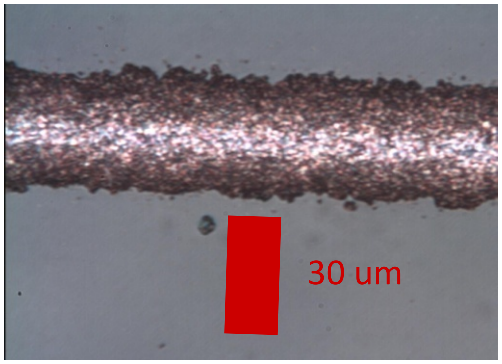
- OPTOMEC® M^3D® printer
- ANI nano-copper ink
- Sintering by OPTOMEC® M^3D laser light
- Kapton® and glass substrates

Optomec/ANI collaboration

- ANI provided its copper nanoparticles inks
- Printing and laser sintering by Optomec M^3D
- Substrates: Kapton and glass



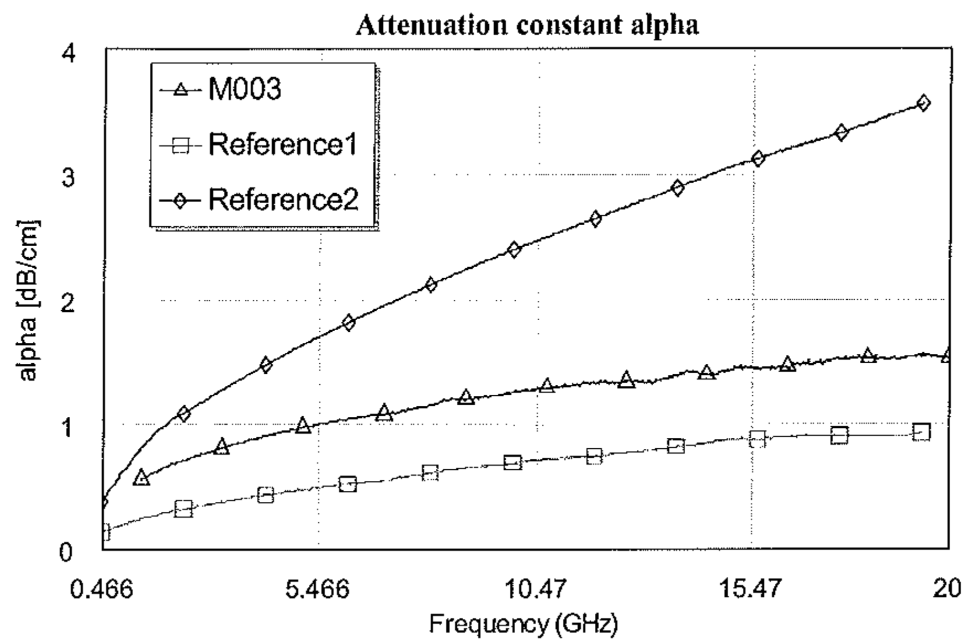
8 µm thick copper on Kapton

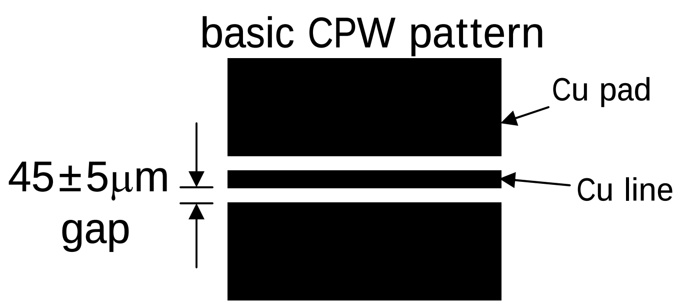


Laser sintered copper ink on glass

Wide band electrical characterization (RF attenuation)

- ANI's Cu ink
  - prototype ink
  - 1.2 μm thick
- Reference1
  - Ag ink
  - 2.6 μm thick
- Reference2
  - Ag ink
  - 1.2 μm thick

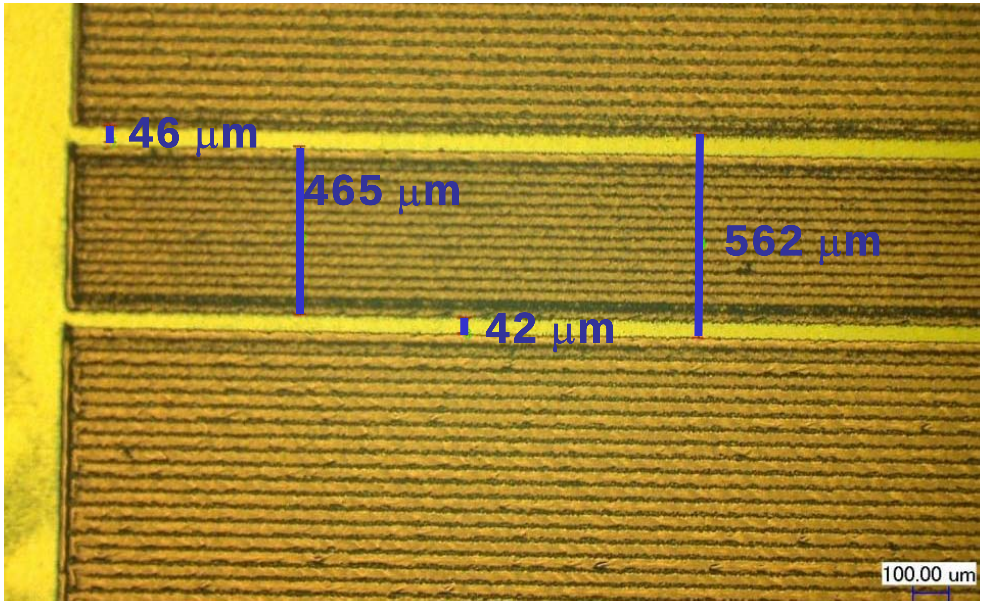




$d_{1/2}$(2.5GHz) = 4 cm
distance for half signal power loss

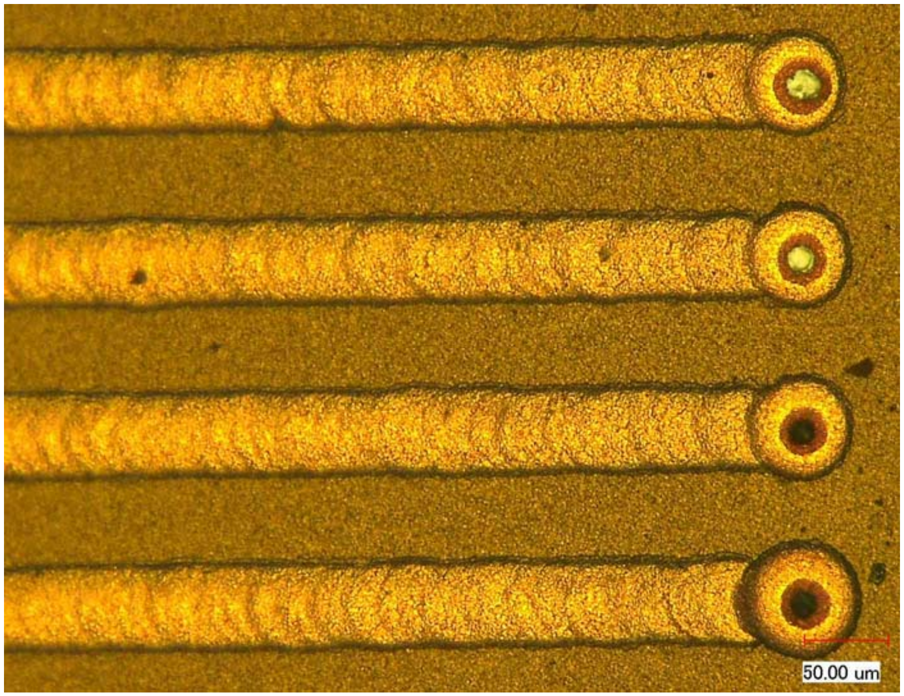
See * on next slide

CPW Cu ink printed using Optomec



* **All the attenuation results were obtained at Tampere University of Technology, Prof. Riku Mäkinen group**

Laser photosintering of Cu ink on silicon



- Wavelength - 830 nm
- Maximum power - 800 mW
- Laser focus diameter - 15 μm
- Heat spread - ±20 μm
- Resistivity - $6x10^{-6}$ Ohm-cm
- Min. line width - 30 μm
- Cu thickness – approx. 2 μm

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Conclusions

- ANI achieved a formulation of copper ink that is inkjettable, the temperature of drying is less or equal to 100 degrees C and the photosintering process does not need inert atmosphere.
- Repeatable copper traces are achieved with resistivity of $3 \times 10^{-6} – 4 \times 10^{-6}$ ohm/cm.
- Initial results show that RF attenuation of traces using the copper ink is comparable if not better that traces using Ag ink.
- ANI secured production of copper nanoparticles, in quantities of hundreds of kilograms per month, suitable for the ink production.

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