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Syringe Dispense Printing of Copper Paste and Formic Acid Vapor Sinter

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Judith M. Lavin, *Marcelino Essien, David M. Keicher, Seethambal S. Mani

*IDS

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Outline

- Copper in Printed Electronics-Why copper
- Direct Write Syringe Dispense Printing of Copper
- Formic acid sintering of Copper
- Experimental setup
- Results
  - Sintering study heating curves
  - Resistance versus temperature
  - Temperature coefficient of resistivity
- Conclusions
- Future work

Why Use Copper in Electronic Industry

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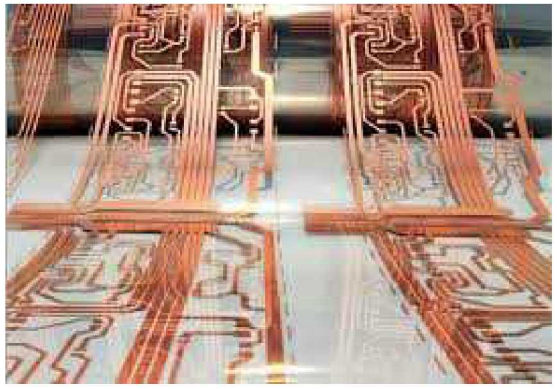
Copper versus Silver or Aluminum

- Copper is cheaper than silver more expensive than aluminum
- Copper is lighter than silver, heavier than aluminum
- Has only a slightly higher resistivity than silver and is less resistive than aluminum
- Copper has lower electromigration relative to aluminum making it more reliable when used in integrated circuits
- Copper is more malleable and ductile than silver and aluminum but just as robust
- Copper can be soldered easier than silver



Direct Write Additive Manufacturing System

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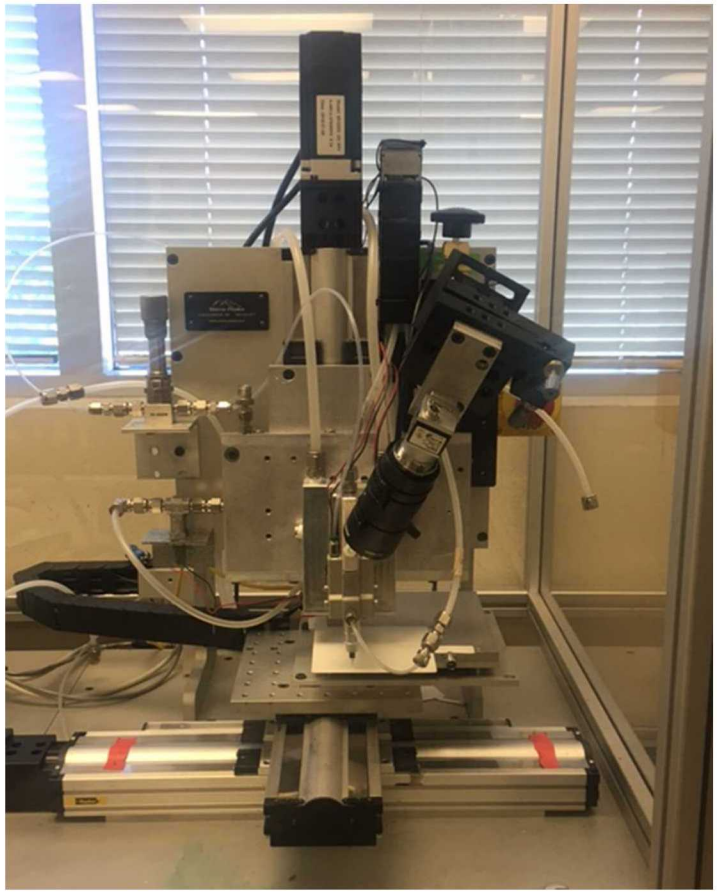
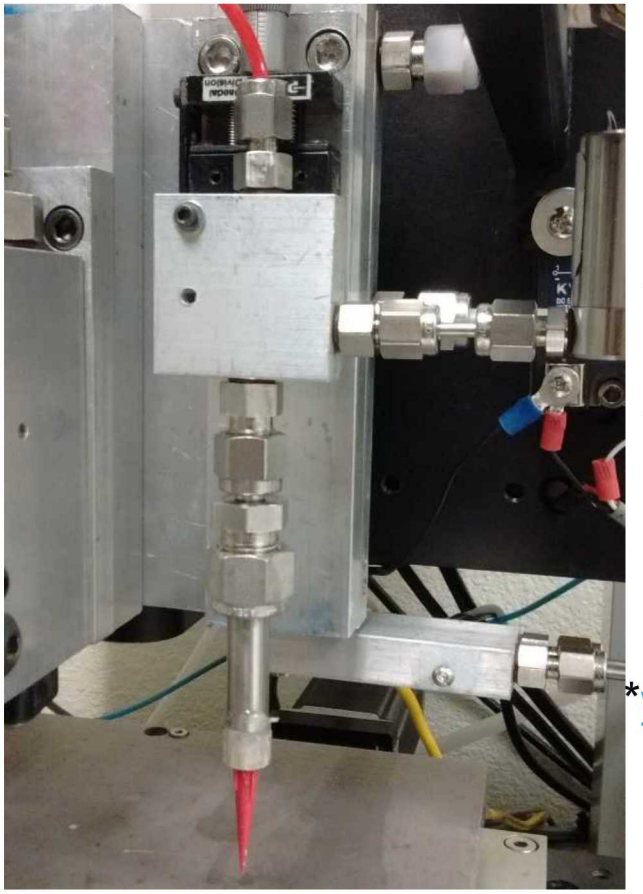
Multi-Material Direct Write System*



Syringe Dispense

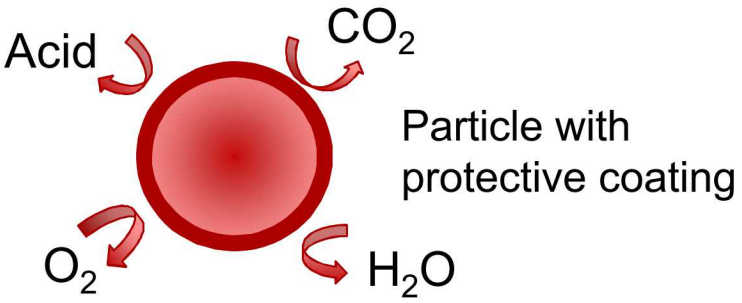


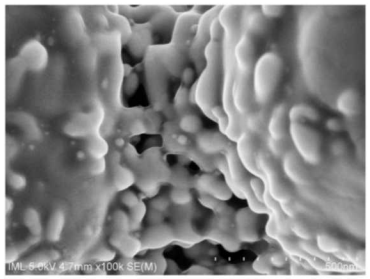
Viscosity: up to 100,000cP
Line width: 50-2000 µm

*www.idsnm.com

Syringe Dispense of Intrinsiq Copper

- Screen print paste CP008 - viscosity 40,000 cp at 10 sec^{-1}, shear thinning
- Composition consists of a mixture of nano and micron sized particles below 10 microns
- Air stable at room temperature until normal atmospheric conditions
- Proprietary coating protects pure nano/micro metal particles from oxidation

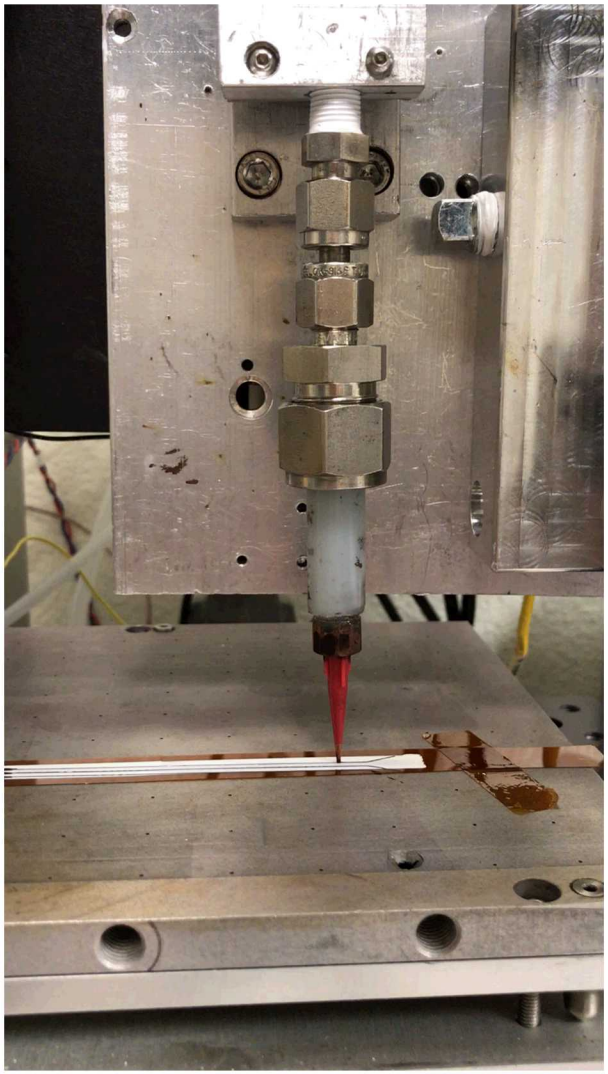


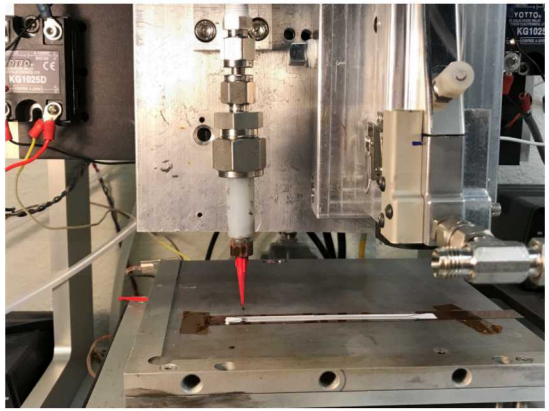


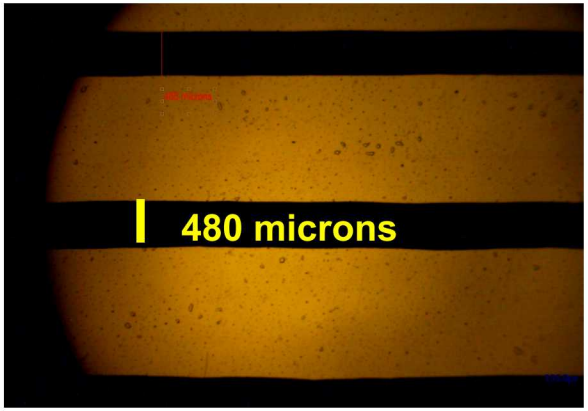
Screen pastes are mixtures of micron & nano copper. Binders are optimized for rheology & adhesion

www.intrinsiq.com

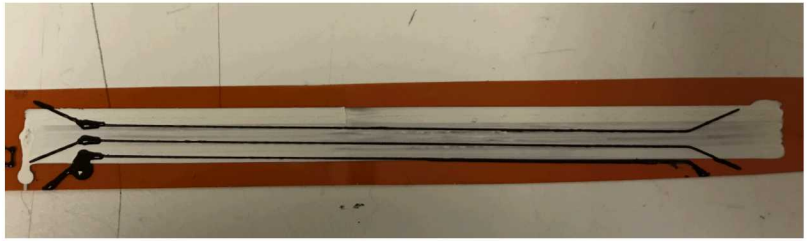
Direct Write – *Syringe Dispense Printing of Copper*







Transmission Mode



Sintering of Copper Paste – Formic Acid Vapors Under Forming Gas

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Why

- **Allows for processing of thicker samples - up to at least 100 microns**
- **Compatible with temperature-sensitive substrates – not necessarily the case with a laser that is short time high energy**
- **Works well with substrates that are highly thermally conductive which draw energy away from print and making it more difficult to sinter with a laser**
- **Suited to sintering features printed over large surface area unlike processing with focused laser beam**
- **Batch process sintering possible – time taken to sinter 1 or 1000 features in fixed area is the same**
- **Considerably cheaper form of sintering compared to laser**

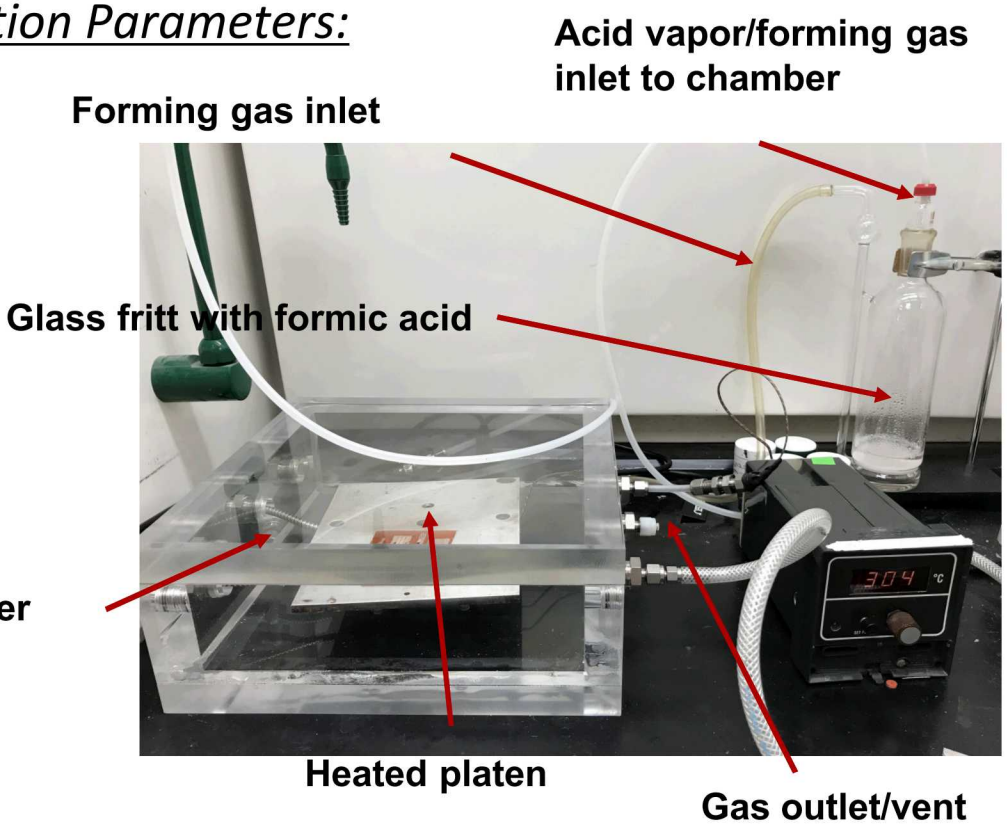
How

- **Substrate is placed in chamber at RT and chamber is purged for 10 minutes**
- **Platen is heated to desired temperature and the substrate is sintered under formic acid vapor/forming gas**
- **Substrate is cooled to ambient temperature in chamber under inert environment**

Print and Sintering Conditions

Copper Syringe Dispense Deposition Parameters:

- Intrinsiq copper: CP008
- Substrate: Kapton- 2mil
- Tip: Nordson 250 micron
- Print speed: 2mm/sec
- Platen temperature: 24C
- Drive Pressure: 0.3 psi



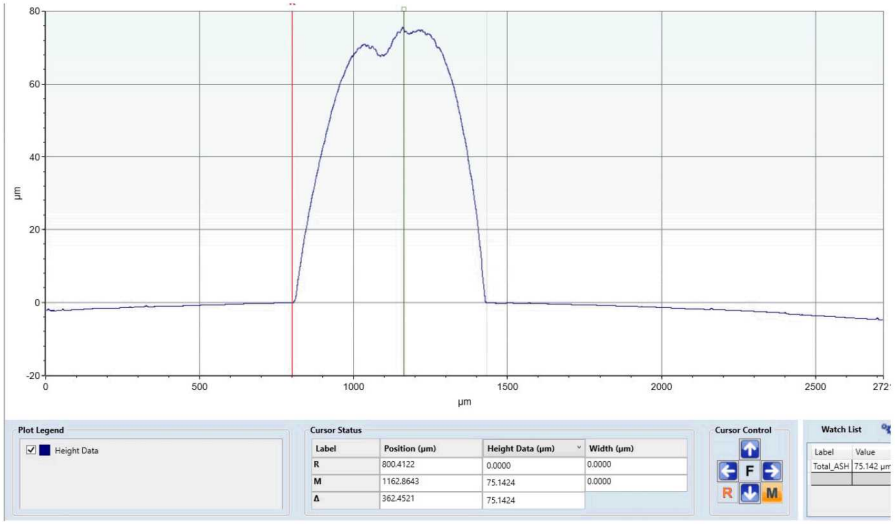
Sintering of Copper

- Formic acid vapor concentration: 10 mmolar*
- Initial sinter temperate: 71C for 120 minutes
- $CuO + CH_2O_2 \rightarrow 2Cu + H_2O + CO_2$
- Probe pads-Creative Materials silver paste; cured at 50C for 80 minutes

Syringe Dispensed Copper - Profiles

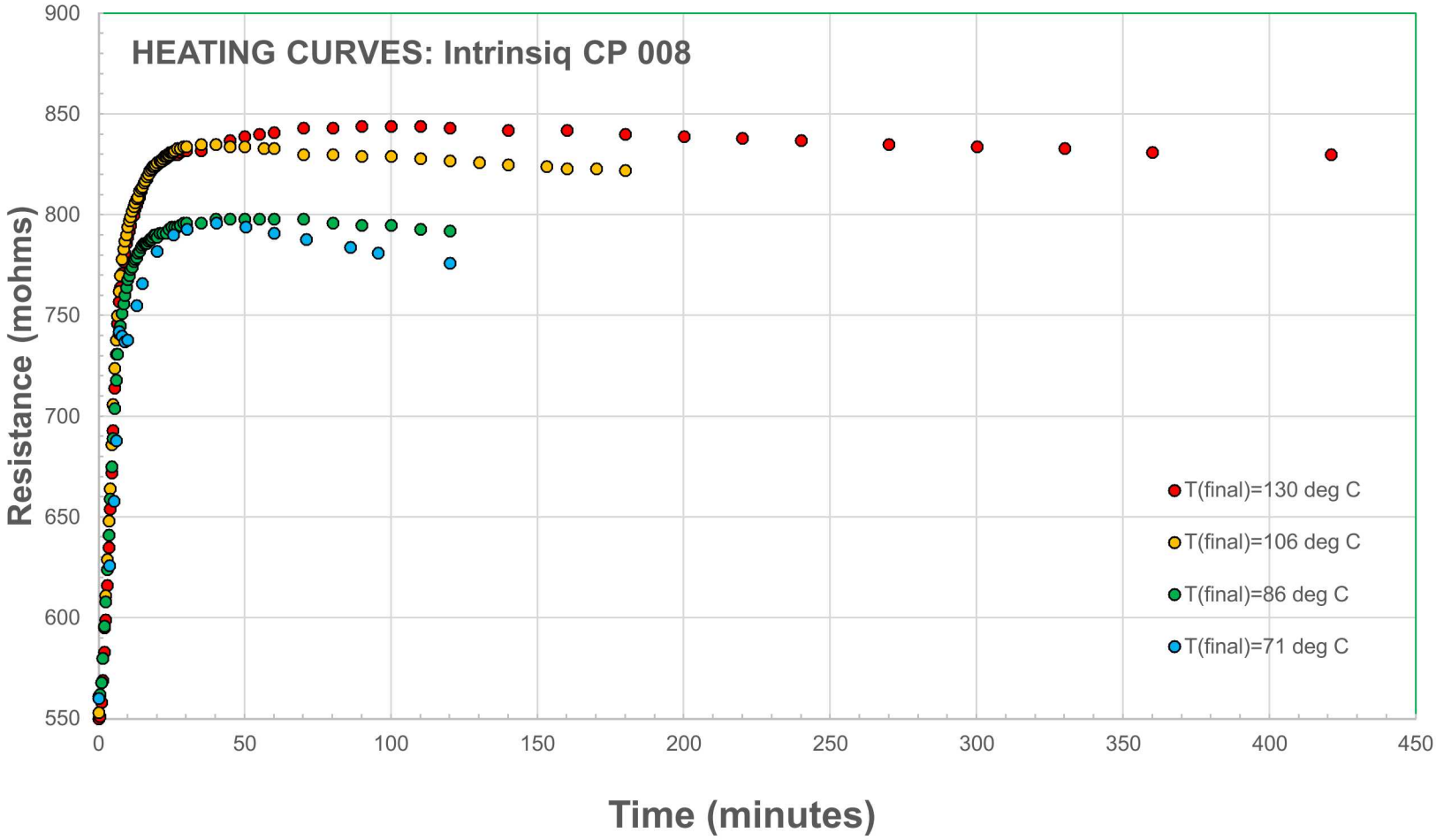
Reflection mode micrograph

Profilometry trace



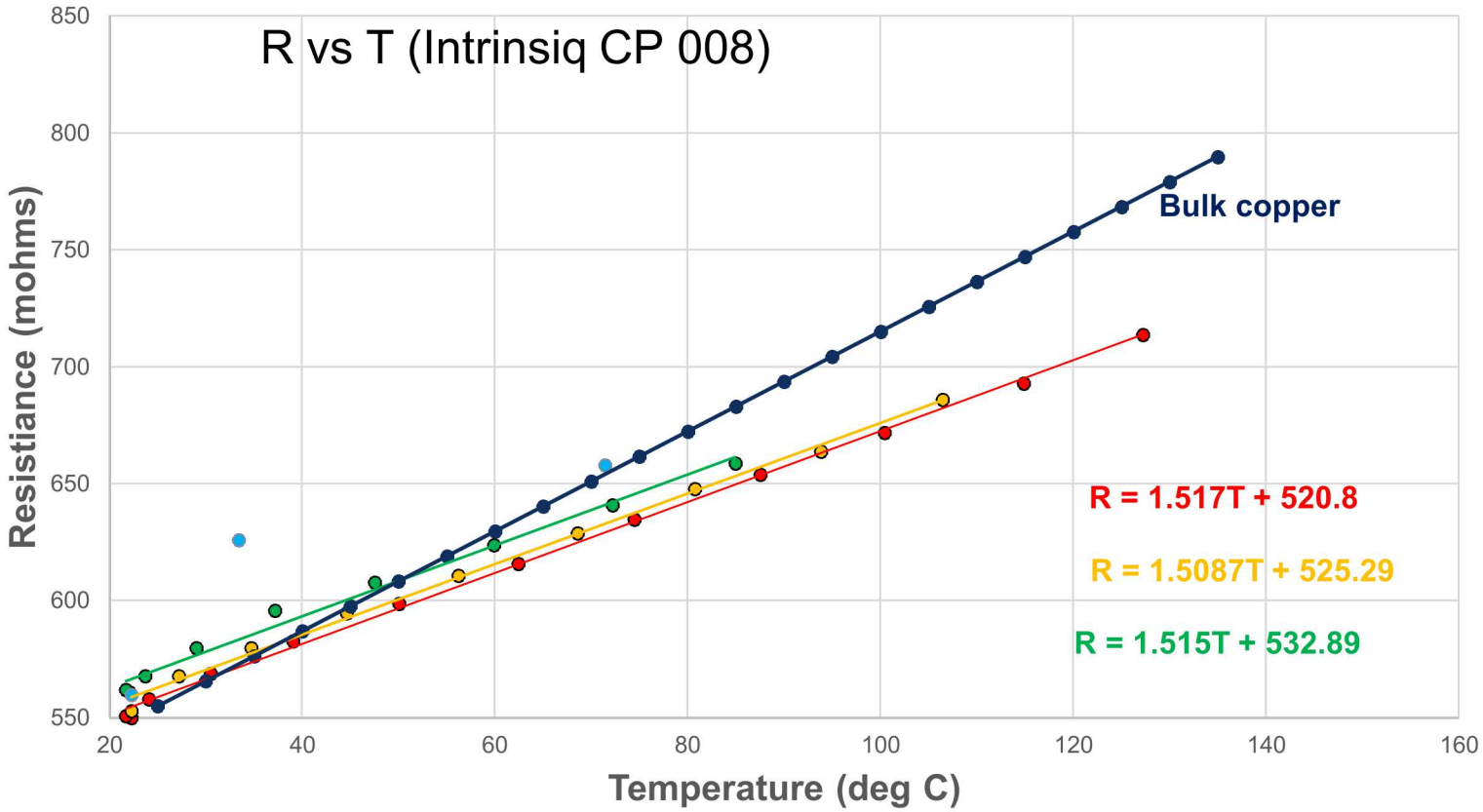
Line length:90mm
Line width: 560 microns
Line height: 80 microns

Sintering Study Heating Curves



Copper trace was originally heated to 71°C to sinter the copper prior to applying probe pads
Resistance still dropping implies copper is still undergoing sintering
At 130 deg C sinter temperature curve plateaus - fully sintered material

Resistance Versus Temperature



- With increasing temperature the resistance increases and is close to linearity
- Good repeatability of the curves over the different heating cycles –consistent
- Pure metals ideal response should be linear

Electrical Propertied of Syringe Dispensed Copper (CP008)

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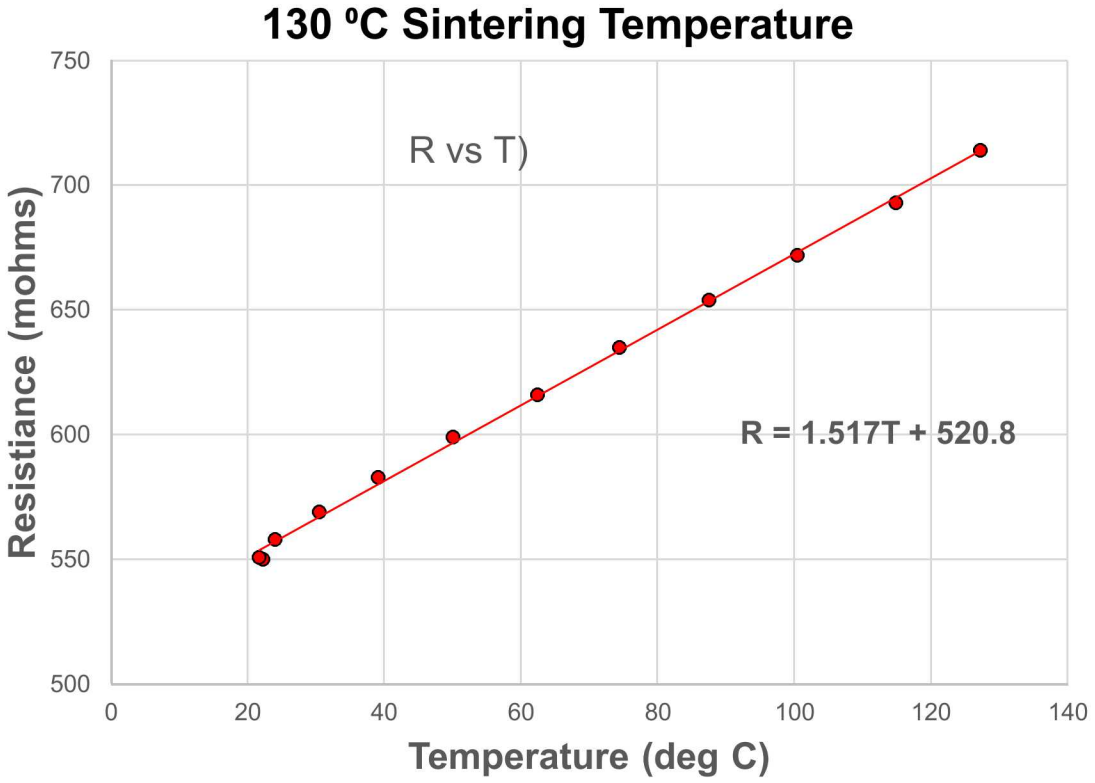
Temperature Coefficent of Resistance (TCR)

$$R = R_0[1 + \alpha(T - T_0)]$$

$$\alpha = \frac{slope}{R_0} \quad R_0 = 550\ mohms$$

Calculated TCR= $2.8 \times 10^{-3}\ ^oC^{-1}$
TCR Bulk Cu = $4.29 \times 10^{-3}\ ^oC^{-1}$



Resistivity:

1.18×10^{-5} ohm cm (Sandia, 4 point probe, 7x bulk)
1.2×10^{-5} ohm cm (Intrinsiq)

Resistivity of bulk Cu: 1.68×10^{-6} ohm cm

Conclusion

- Have demonstrated ability to Direct Write print copper under ambient conditions
- Low temperature sintering under formic acid vapor/forming gas
- Sintering of copper using formic acid is amenable to processing thick samples
- TCR for DW copper is less than that of bulk copper as expected
- Resistivity measured matches that reported by Intrinsiq validating the results of our DW printing and formic acid processing of copper
- Achieved a resistivity of 7X bulk copper

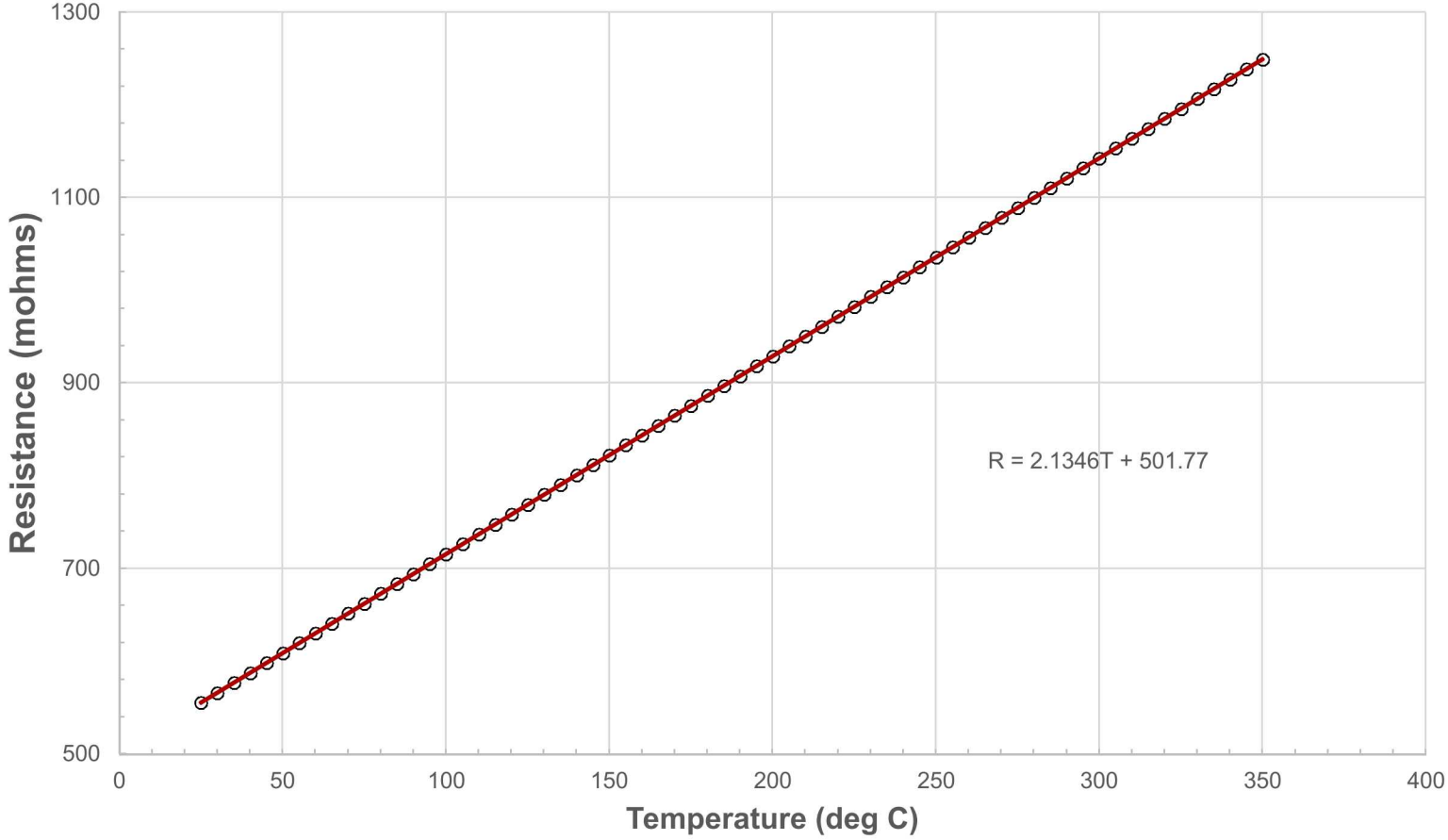
Future Efforts

- Investigate by how much the time required to achieve a fully sintered part can be reduced by increasing the temperature
- Gain a better understanding into exact relationship between formic acid vapor concentration and sintering time in relation to resistivity
- Explore other sources of copper and deposition substrates
- Optimize process to get resistance as close to bulk as possible
- Printing and testing of components

THANK YOU!

Funding: Sandia National Laboratories LDRD Office

Temperature Coefficient of Resistivity – Pure Copper



$$R = R_{ref}\,[1 + \alpha(T - T_{ref})]$$

Where,

R = Conductor resistance at temperature "T"

R_{ref} = Conductor resistance at reference temperature T_{ref}, usually 20° C, but sometimes 0° C.

α = Temperature coefficient of resistance for the conductor material.

T = Conductor temperature in degrees Celcius.

T_{ref} = Reference temperature that α is specified at for the conductor material.