Roadmap for Copper Sintering - Next Interconnect for Power Electronic Module Packaging

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Infineon

OSRAM

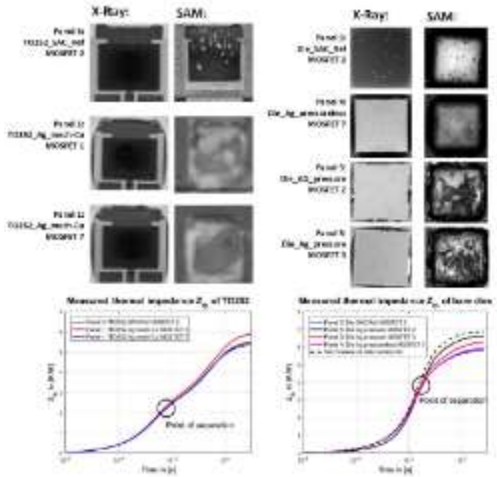
Audi

BMW

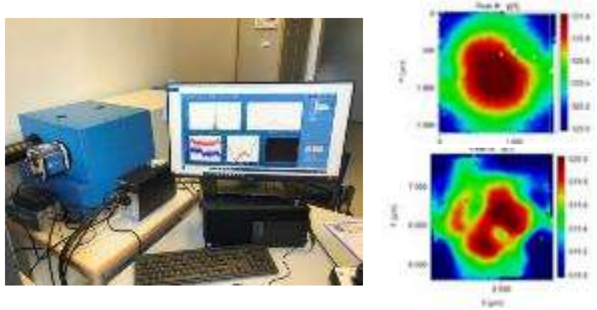
Technische Hochschule Ingolstadt

Introduction

- **Microelectronics packaging research group of the Institute of Innovative Mobility at Technische Hochschule Ingolstadt (THI)**
  - Process development of fluxfree soldering and sintering
  - Paste development (Fluxfree solder pastes, copper sinter paste, copper inks)
  - Reliability and lifetime testing
  - Test equipment development, e.g. Transient thermal analysis (TTA)
  - Modelling (Finite Element and Machine Learning)
- **Copper Sinter development projects started 2017**
- **Since 2019 research cooperation with Schlenk (metal pigments and copper foils)**
- **2022 CuNex was founded as Joint Venture between researchers from THI (CEO Krishna Bhogaraju) and Schlenk**



Detection of crack formation by TTA and Scanning Acoustic Microscopy (SAM)



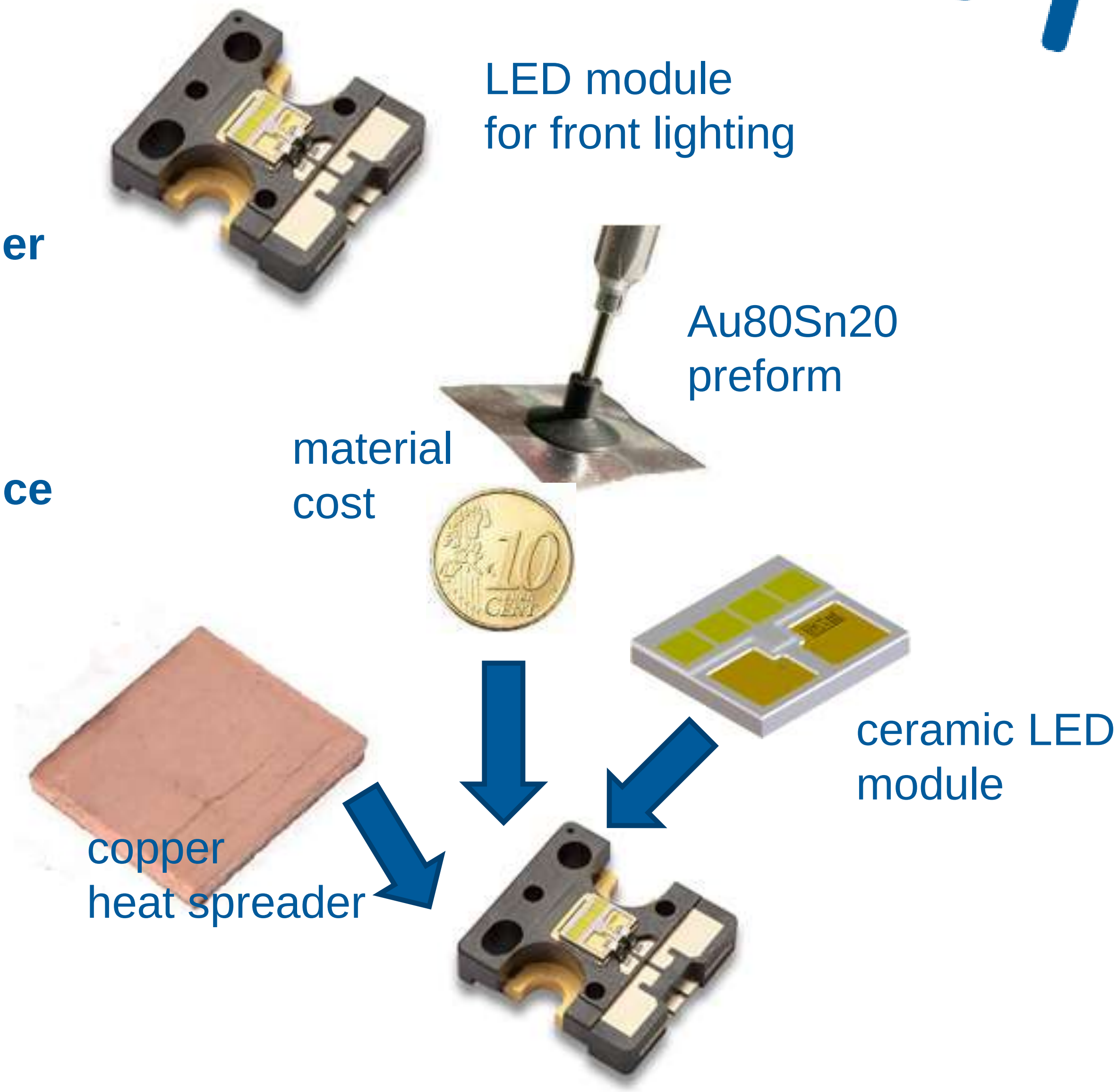
RAMAN Strain measurement in semiconductor

Content

Personal Motivation from 2008 @ Philips/Lumileds

Introduction

- **For heat management of high power LEDs ceramic carrier is mounted on copper heat spreader**
- **Due to thermomechanical mismatch of copper and ceramic large thermomechanical stress**
- **AuSn used as solder with high fatigue resistance (yield strength 200MPa)**
- **Silver Sintering lower reliability (in that time)**
- **Replacing AuSn solder by copper paste**
- **Process requirement:**
  - Temperature < 320°C
  - Time < 30s



Motivation

Introduction

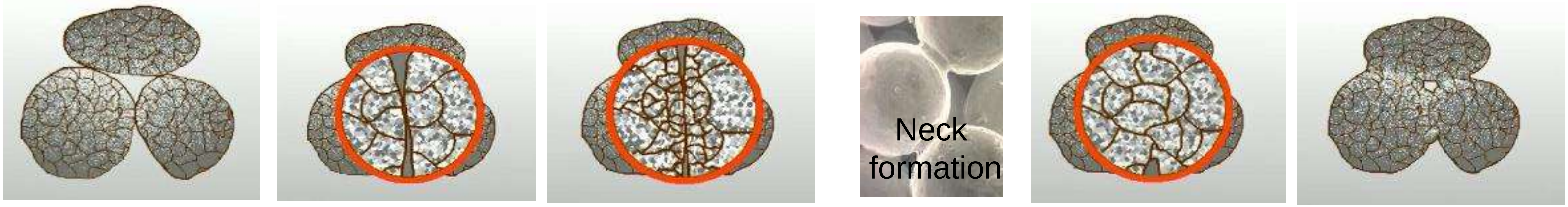
- **Sintering – Well known technology for primary shaping**

Metal Powder

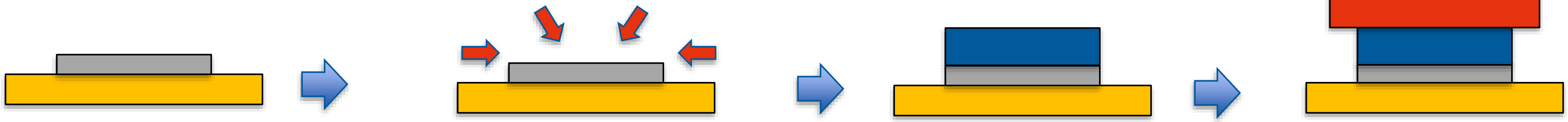
Force: Deformation →
Contact area increased

Temperature: Diffusion
→ Recrystallization

Interconnect



Sintering under pressure in chip interconnect technology



Paste printing

Heat

Pre-Drying of the paste

Pick and Place of the component

Pressure & heat

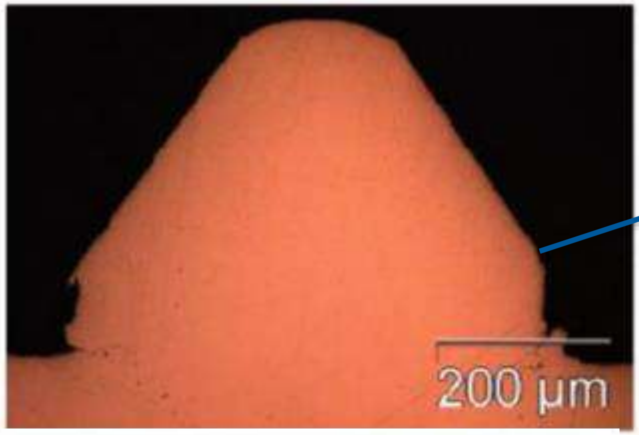
Heat

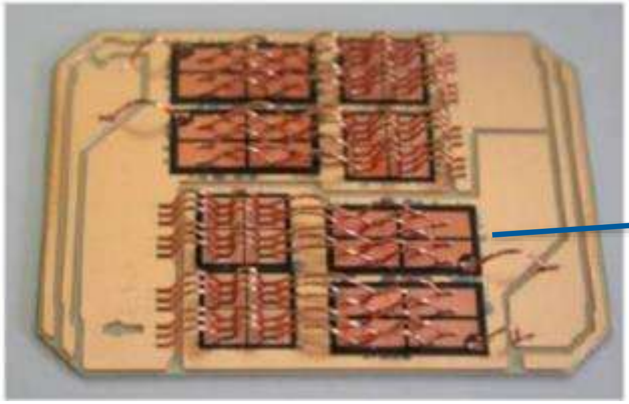
Sintering under force

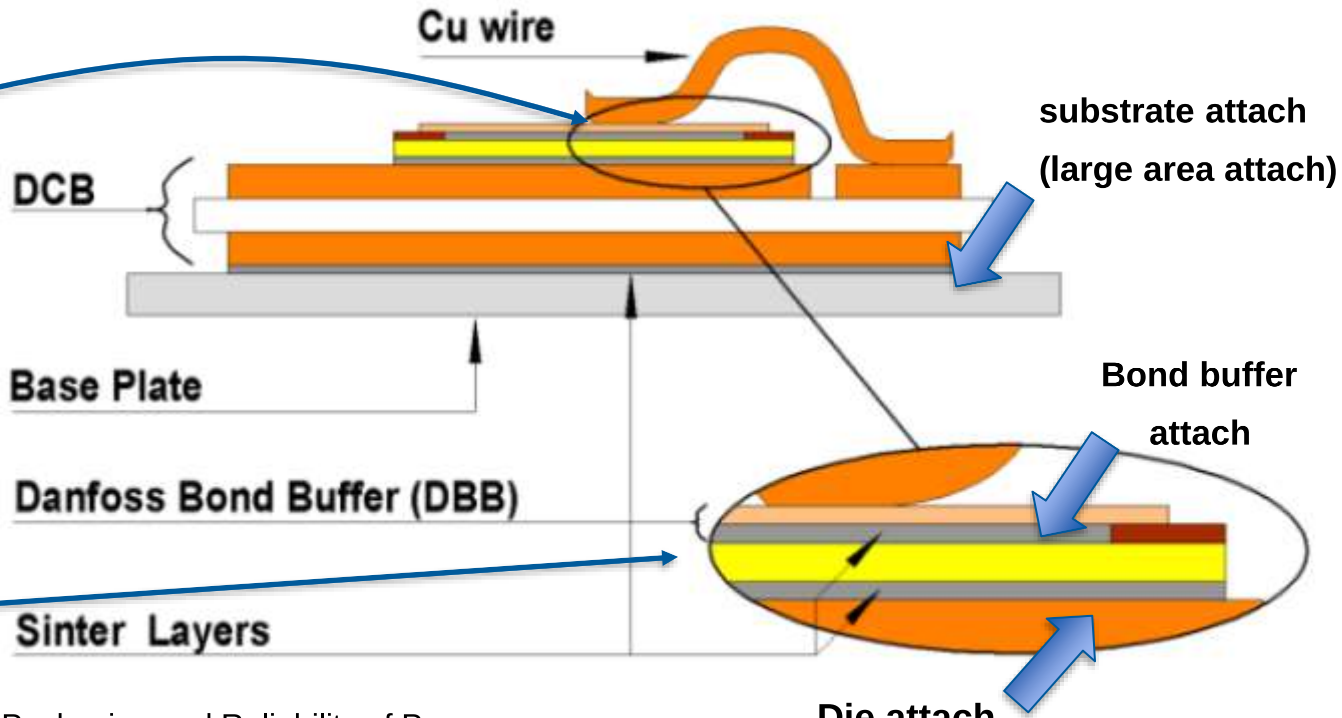
Standard Modul

Introduction

- **Example design of Power electronic module with three sintered interconnects**





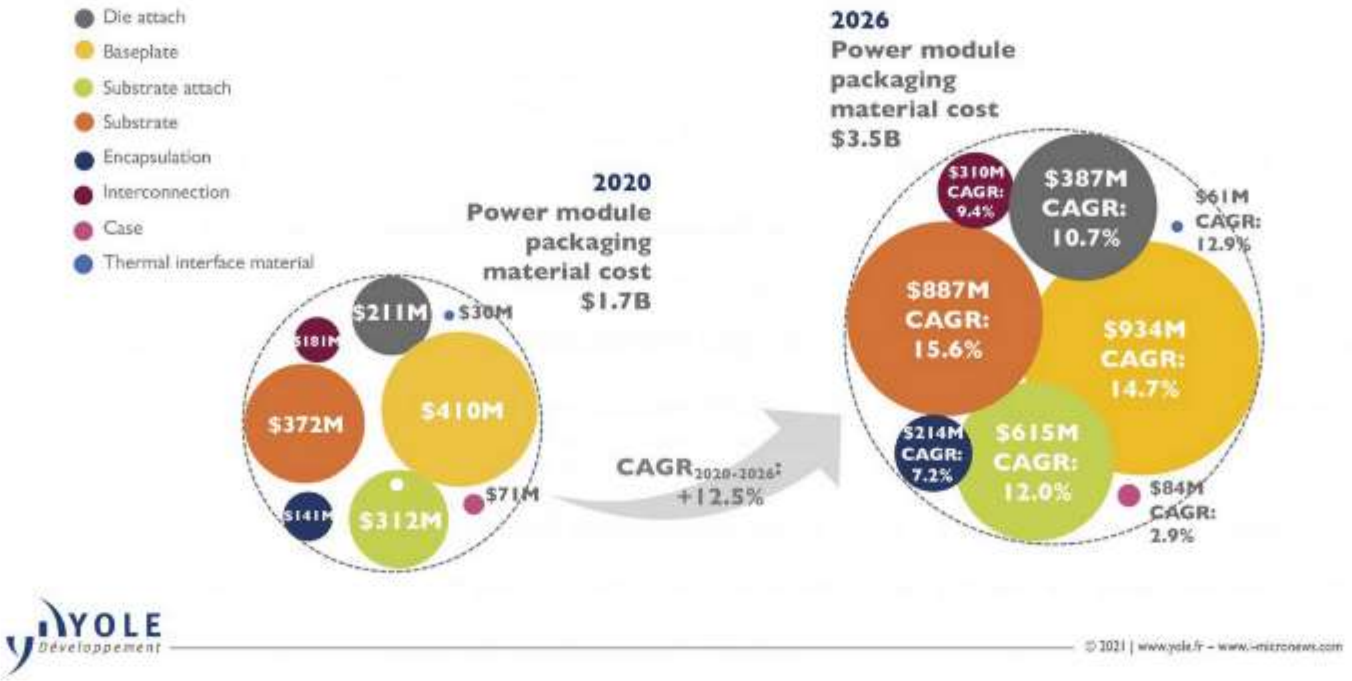


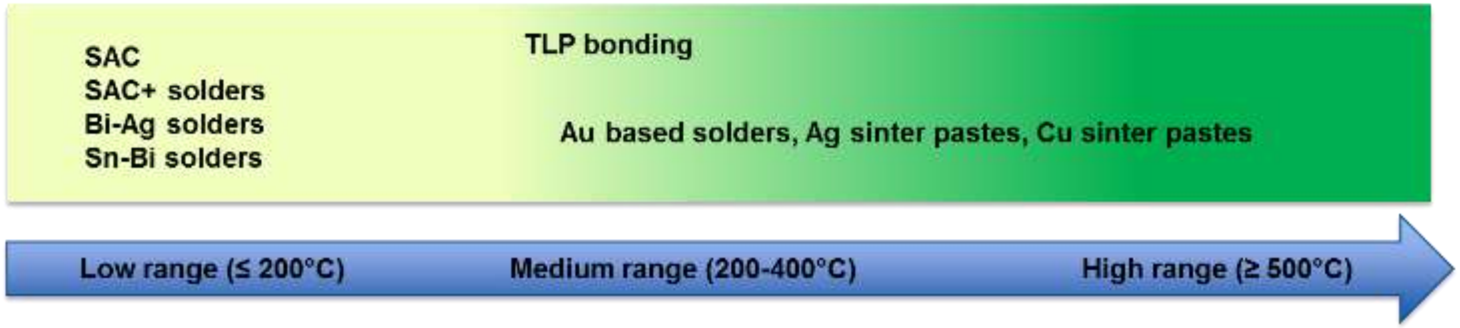
J. Lutz, Packaging and Reliability of Power Modules, CIPS 2014, Nürnberg

(Danfoss)

Power Module Packaging Market

Introduction





SAC
SAC+ solders
Bi-Ag solders
Sn-Bi solders

TLP bonding

Au based solders, Ag sinter pastes, Cu sinter pastes

Low range (≤ 200°C) | Medium range (200-400°C) | High range (≥ 500°C)

- **The die- and substrate-attach material industry is expected to grow significantly in size**
- **Driving forces**
  - Rapid pace of electrification in the automotive industry (vehicles and charging infrastructure)
  - Renewable power sources are major driving forces.
- **New cost-effective die-attach materials are needed that are as reliable as Ag and sustainable**

Comparison Copper and Silver

Introduction

- **Cu offers both a substantial cost advantage over Ag and comparable mechanical and thermal properties.**
- **Challenges**
  - Oxidation of Cu particles
  - Higher sintering temperature

Primary silver production requires significant more energy

Property (unit)	Ag	Cu
Cost ($/kg)	500	5
Abundance in earth's crust (ppm)	0,08	50
Thermal expansion (µm/mK)	429	401
Elastic modulus (GPa)	83	120
Bulk modulus (GPa)	100	140
thermal conductivity (W/mK)	429	400
Melting point (°C)	962	1085
Embodied Enegrgy (MJ/kg)	1500	100

Status Silver and Copper Sintering

Paste and Processes

- Ag sintering in elctronics started in the 1990th with the patents and research work from H. Schwarzbauer in 1989
- Ag sintering under pressure was introduced in manufacturing and can be considered as a mature technology
- However, standardization in the process compared to SMD soldering is very low
- Presserureless, Ag sintering based on nanoparticles followed when nano powder got available and is now in productions since more than 5 years
- Intense research work was ongoing in the last five years on copper sintering
- Paste is available since roughly three years (engineering materials)
- Nowadays, copper sintering in the evaluation and design-in for new product generations

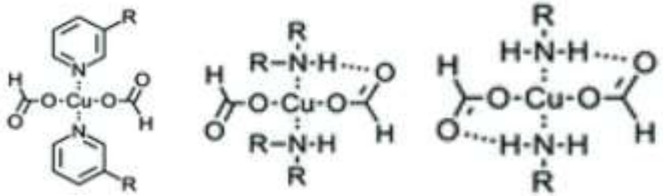
Copper Sinter Materials

Paste and Processes

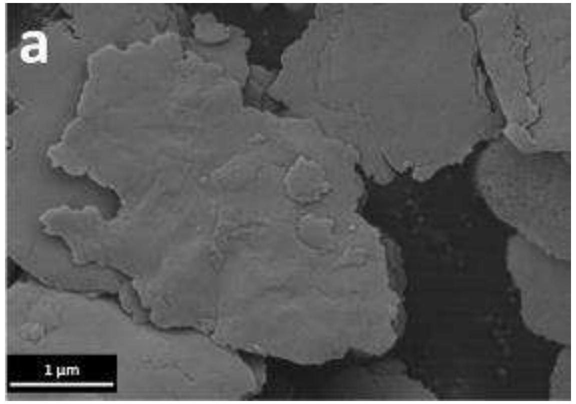
Similar to silver particles

- **Micro particles: flakes or spheres**
- **Nano particles**
- **Metal salts (particle free)**

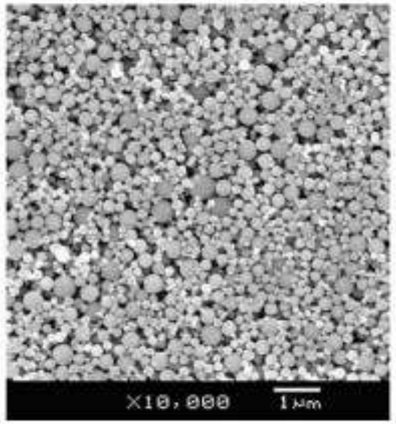
copper formate $Cu(HCOO)_2$,
copper acetate $Cu(CH_3COO)_2$,
copper oleate $Cu(C_{17}H_{33}COO)$



- **Atomic Metal is produced and forms particles**



Copper Flakes (200nm thickness)



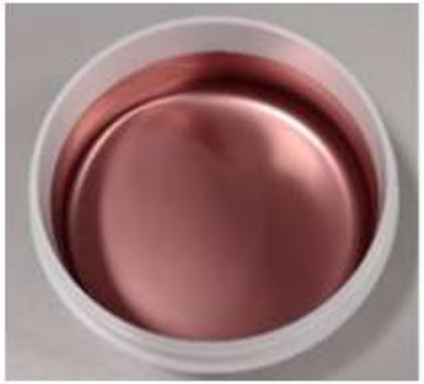
Nano particle

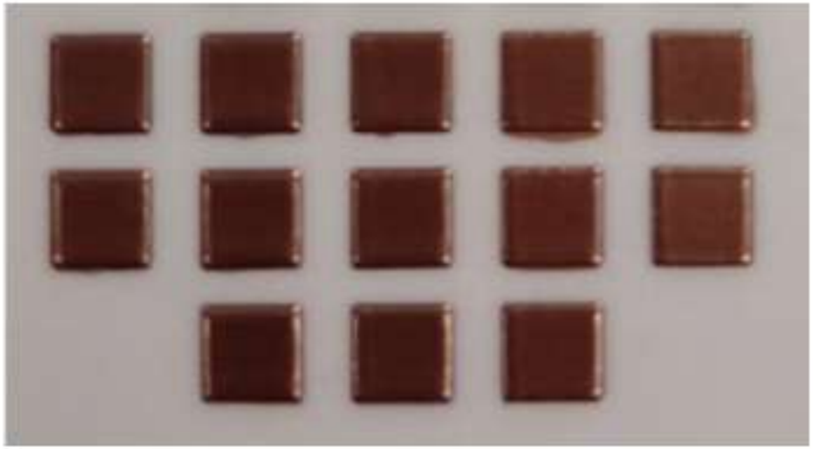
- **Metal particles need surface protection/coating to protect surface, e.g. oxidation, and hinder agglomeration and sintering of particles before the interconnection process**

Sinter Process

Paste and Processes

- **Binder contains composition to**
    - provide printability
        - Mixture low and high boiling fluids
    - realize activation at defined sinter temperature
        - particle surfaces
        - sinter pads
    - reducing agents
    - prohibit agglomeration
    - prohibit blead out
- **Binder evaporates residual free at sinter temperature**
- **Required pot life**





Schlenk copper paste (THI / CuNex inside)

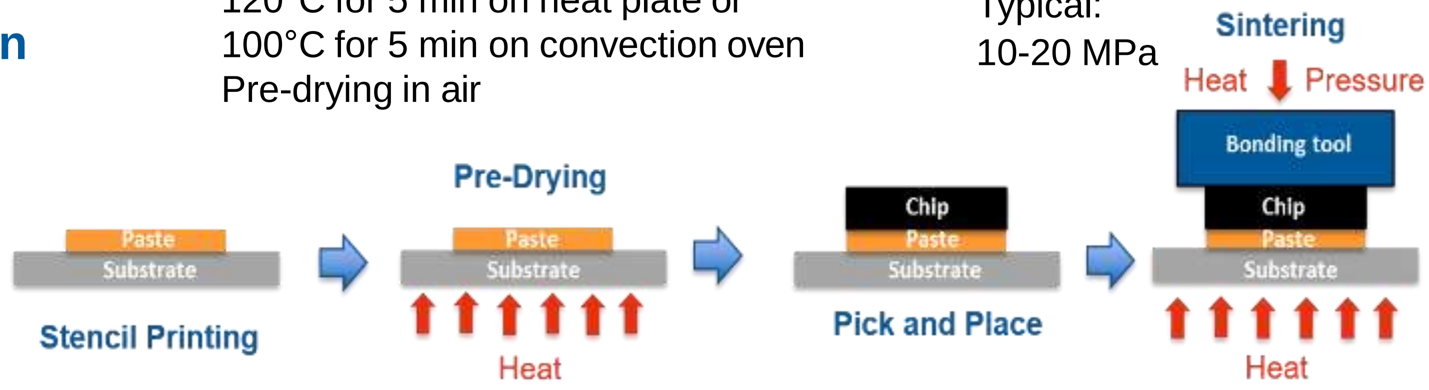
Sinter Process Sequence

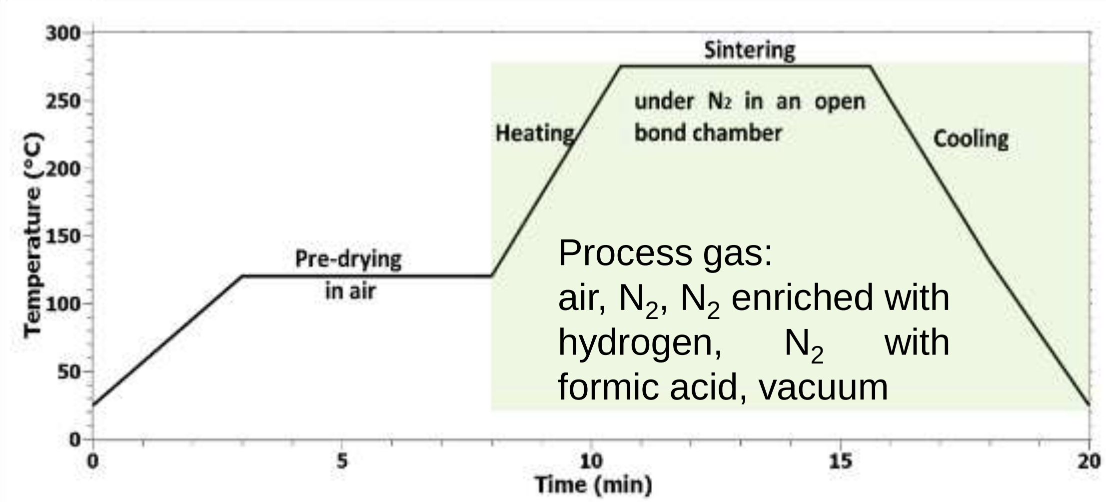
Paste and Processes

- **Paste /Material application**
  - Stencil and screen printing
  - Dispensing
- **Predrying**
  - paste is fully dry
  - paste still slightly sticky
- **Pick and Place (P&P)**
  - applying tacking agent and P&P
  - preponding with hot tool and force
  - P&P still sticky paste
- **Sintering**
  - Closed or open bond chamber (residual oxygen)
  - Stamp tool and press technology

120°C for 5 min on heat plate or
100°C for 5 min on convection oven
Pre-drying in air

Typical:
10-20 MPa





Process gas:
air, N_2, N_2 enriched with hydrogen, N_2 with formic acid, vacuum

- **Processes are presently still considered as IP.**
- **When will be a standardization for the process ?**
- **It would be better soon!**

Copper Sinter Paste – the commercial landscape

Copper Paste and Processes

Most important (but non exhaustive) list of suppliers … more are coming.

Company	**Particles size**	**Sintering time (min)**	**Sintering temperature (°C)**	**Sintering pressure (MPa)**	**Controlled atmosphere**	**Shear strength (MPa)**
Heraeus	Micro Cu	5	325	20	Yes	30
Indium Corporation	Nano Cu	15	240	0	Yes	17
Showa Denko	Nano Cu	5	280	9	Yes	80
Mitsui Mining	Nano Cu	60	200	0	Yes	60
Kuprion	Nano Cu	<8	200-230	NA	NA	NA
CuNex P1	Micro Cu	5	275	10	No	60
CuNex P2	Cu salt	5	250	20	No	100

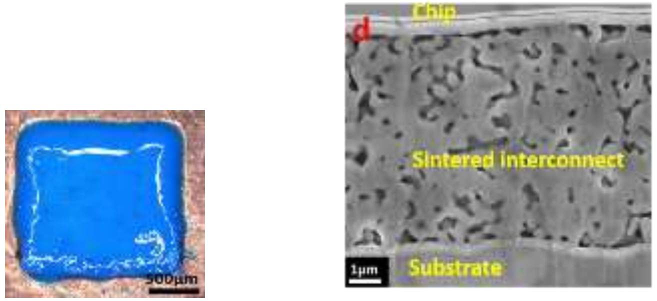
Status: partly commercial product - partly available engineering sample

Copper Paste Building Block System

*Copper Paste Development @ **THI***

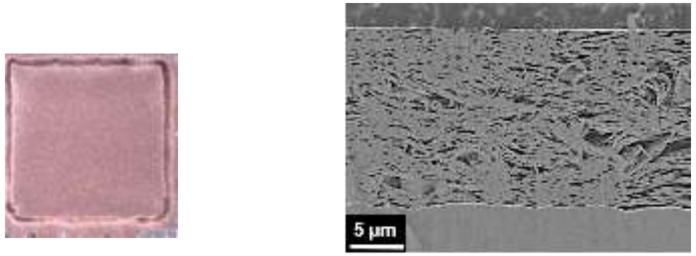
Cu salt based sinter paste

Suitable for bondline thickness requirements < 10 µm and bulk-like sintered interconnects.



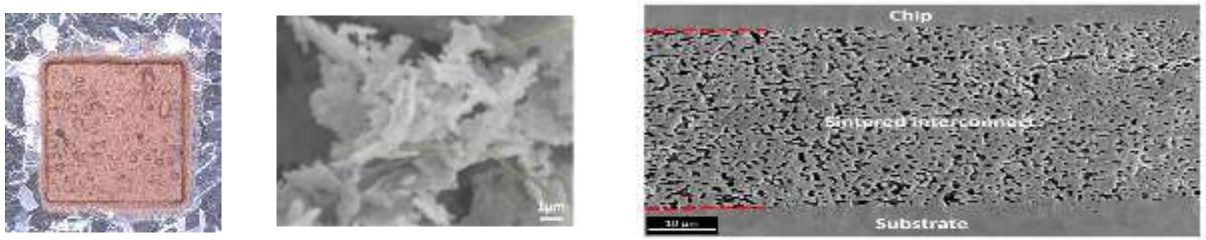
Cu flake based sinter paste

Stacked Cu flakes with pores oriented parallel to the interconnect. Easily deformable flakes to compensate surface roughness & near “zero” porosity under high pressure sintering



Surface modified brass flakes based sinter paste

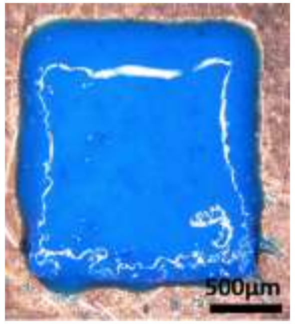
Tunable porosity & young’s modulus for application specific requirements



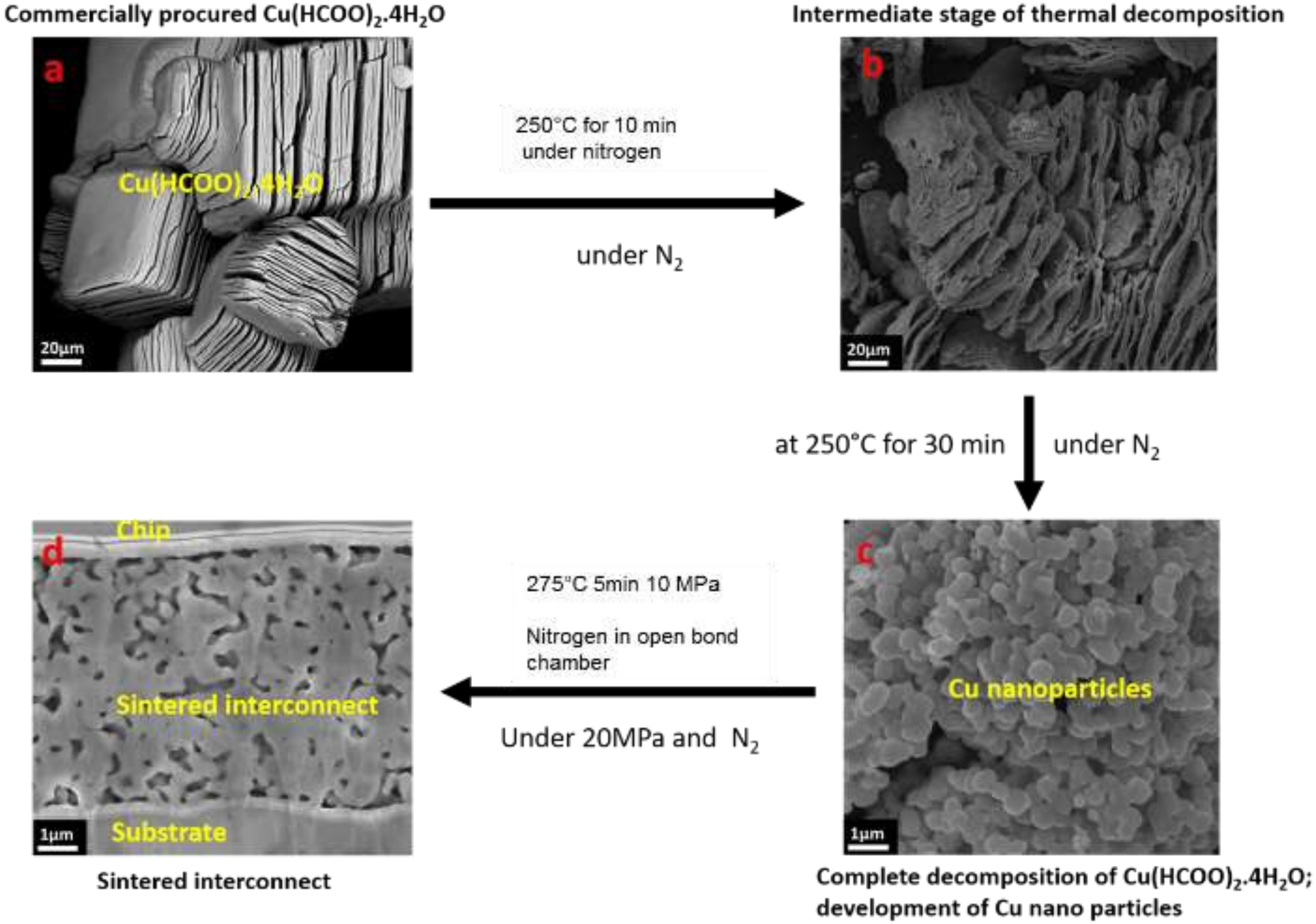
Copper Salt Paste

*Copper Paste Development @ **THI***

Cu salt based sinter paste



- Sinter paste based on Cu(II) formate tetrahydrate.
- Cu nanoparticles generated in-situ during the sintering process by thermal decomposition of Cu(II) formate.
- Suitable for bondline thickness requirements < 10 µm and bulk-like sintered interconnect.
- By adding complex builders (e.g. amino-2-propanol and hexylamine) the decomposition temperature can be reduced



Commercially procured $Cu(HCOO)_2.4H_2O$

250°C for 10 min under nitrogen

under N_2

Intermediate stage of thermal decomposition

at 250°C for 30 min under N_2

Complete decomposition of $Cu(HCOO)_2.4H_2O$; development of Cu nano particles

275°C 5min 10 MPa

Nitrogen in open bond chamber

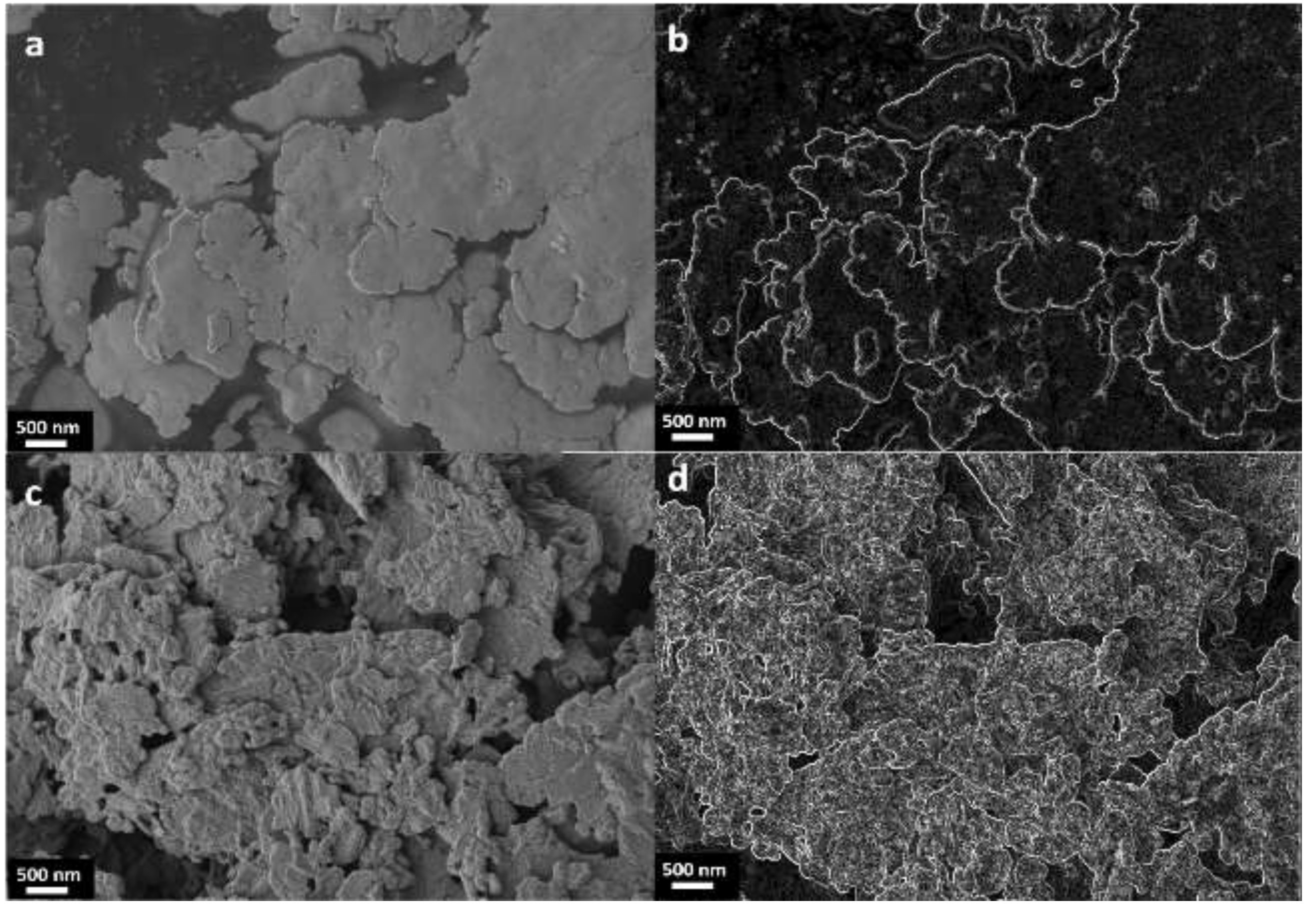
Under 20MPa and N_2

Sintered interconnect

Nanostructured Brass Flakes

*Copper Paste Development @ **THI***

- As low cost initial ball grindes brass flakes (30%Zn and 7%Zn) were used as initial material (below 100€/kg)
- Etching with 12 M HCl for 4 hours while stirring at 600rpm at room temperature
- SEM images of the Cu-alloy powder (a) before etching and (c) after etching. Surface and edge detection by open source imagej software (b) before etching and (d) after etching.

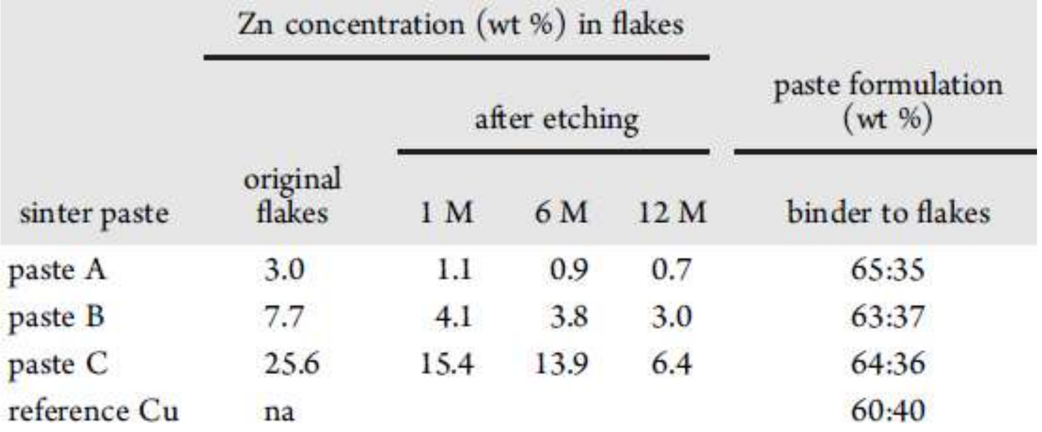


Cu7%Zn after 4h etching

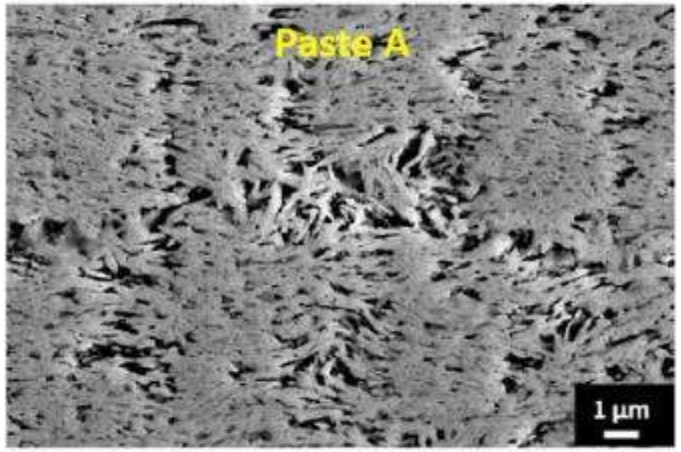
Dependence initial Zn Content of Brass Flakes

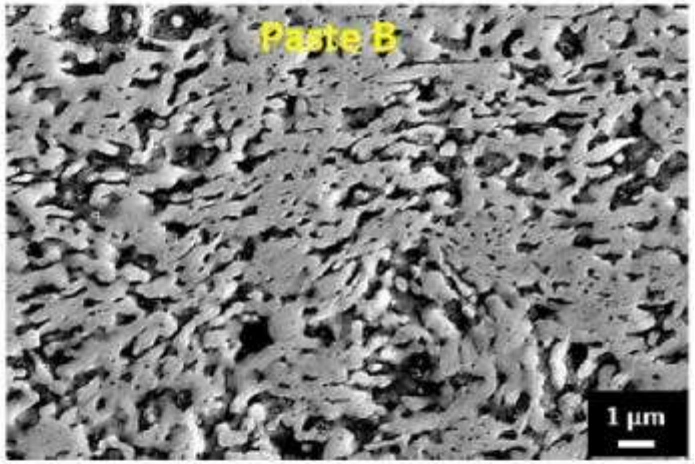
*Copper Paste Development @ **THI***

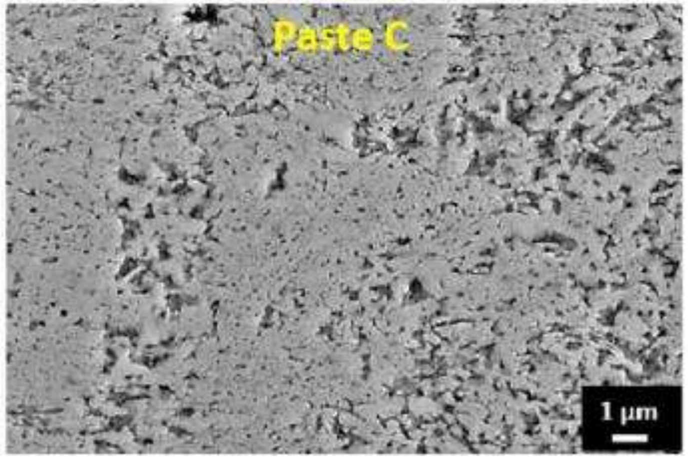
- **SEM images of the microstructure of the pastes A, B, and C sintered at 275 °C for 5 min under 10 MPa.**
- **Porosity can be adjusted by etching**



	Zn concentration (wt %) in flakes				
		after etching			paste formulation (wt %)
sinter paste	original flakes	1 M	6 M	12 M	binder to flakes
paste A	3.0	1.1	0.9	0.7	65:35
paste B	7.7	4.1	3.8	3.0	63:37
paste C	25.6	15.4	13.9	6.4	64:36
reference Cu	na				60:40



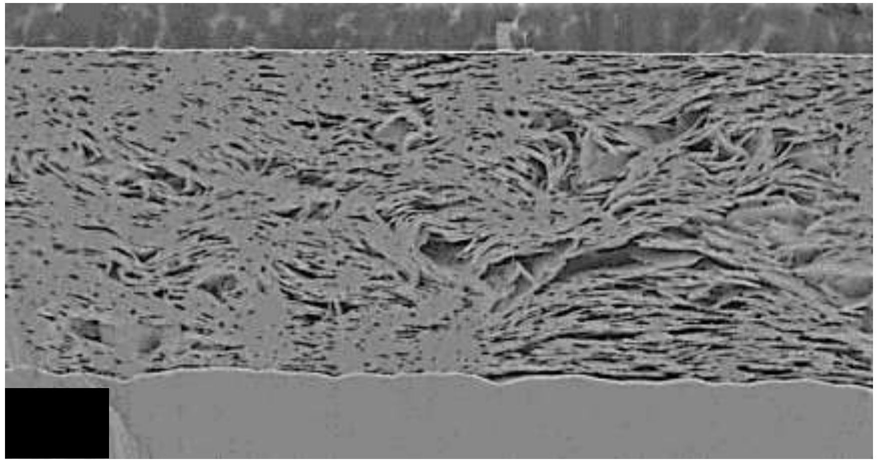




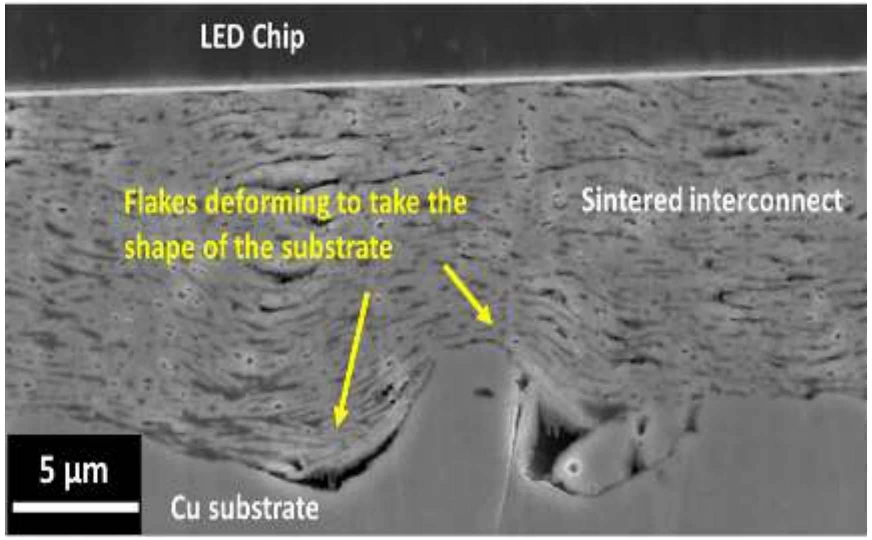
Stacked Copper Flakes

Copper *Paste* ***Development @ THI***

- Sintering @ 275^{o}C and 20 MPa bonding pressure.
- Porosity < 20%
- Shear strength > 50 MPa.
- Proven performance of >1 million power cycles at ΔT135K
- Suitable for die-attach bonding and substrate attach (large area bonding)

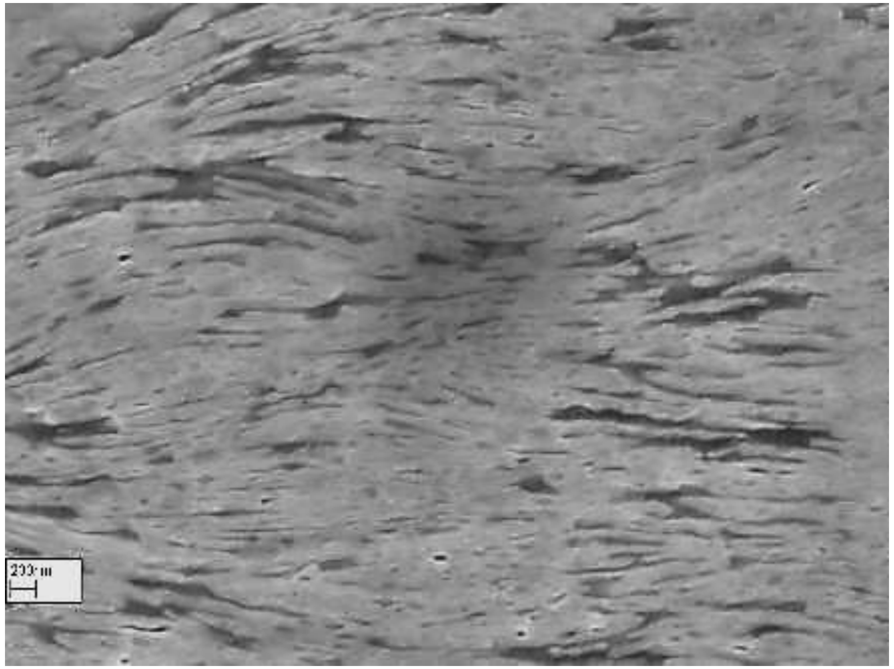


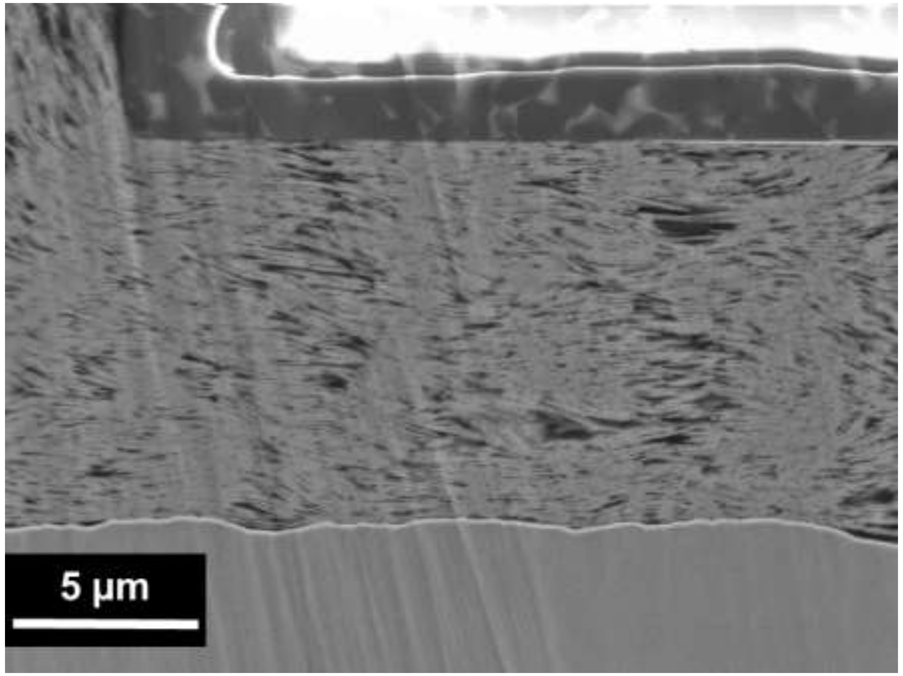
- Capability of the flakes to bend along surface roughness/irregularities



Stacked Copper Flakes

*Copper Paste Development @ **THI***





- **Flakes stack over each other and show readiness to sinter together.**
- **Interconnect is dominated by long, thin interconnected pores.**
- **Very good sinterability to chip and substrate metallization and edges.**

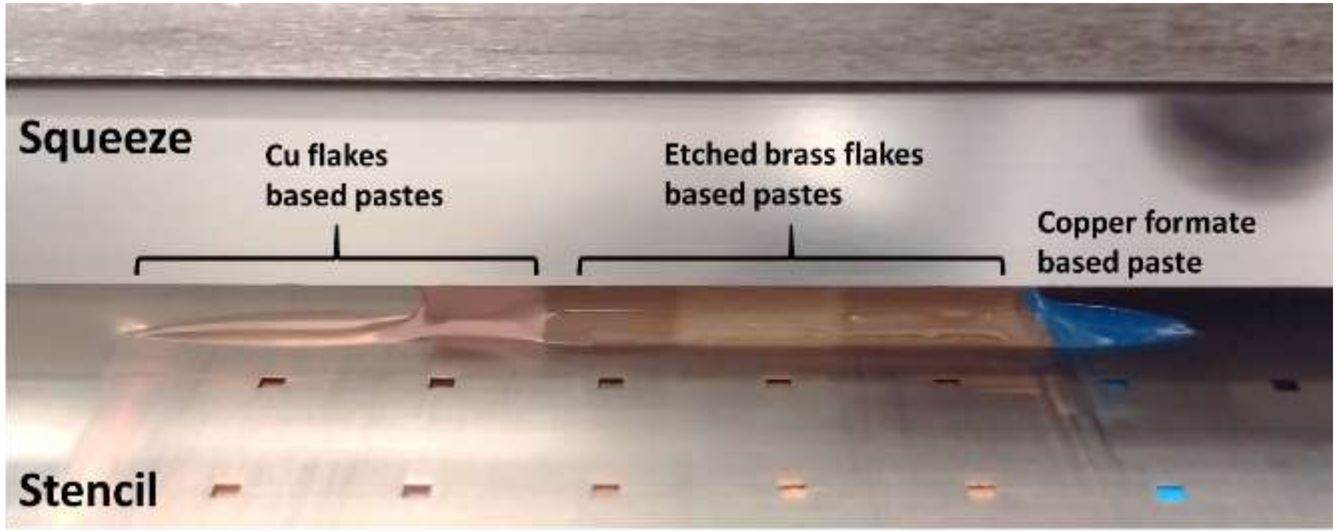
Stencil Printing Capabilities & Parameters

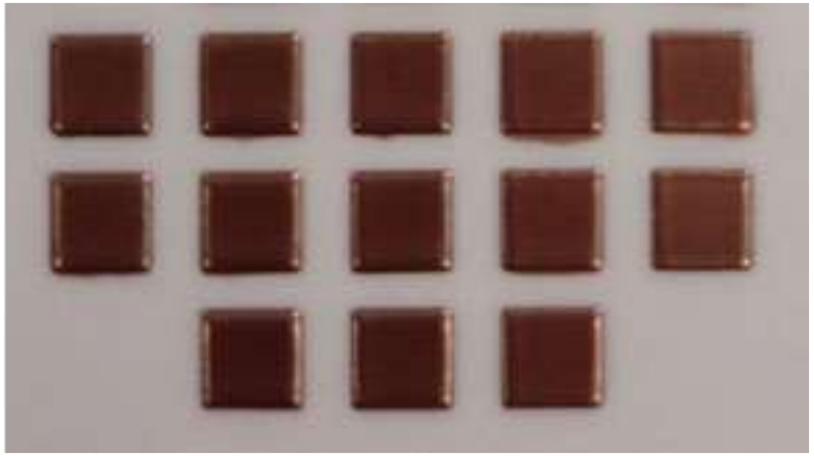
Copper Paste Development @ THI

- **Paste shows very good workability & stencil/screen printing capabilities.**
- **Easy separation from the stencil and squeeze & very good form adherence.**

- **Storage at room temperature for 6 months.**
- **Mixing by a planetory rotary mixer for 5 min at 500 rpm before usage.**
- **Stencil printing**

Print results: Semi-automatic stencil printer (PBT, Go3v) with a motorized double blade squeegee and a stencil thickness of 75 µm. Squeegee speed was 13 mm/s, squeegee pressure 20 N and the stencil separation 2.3 mm/s.





Status: THI Copper Paste Compared to Silver Paste

Copper Paste Development @ THI

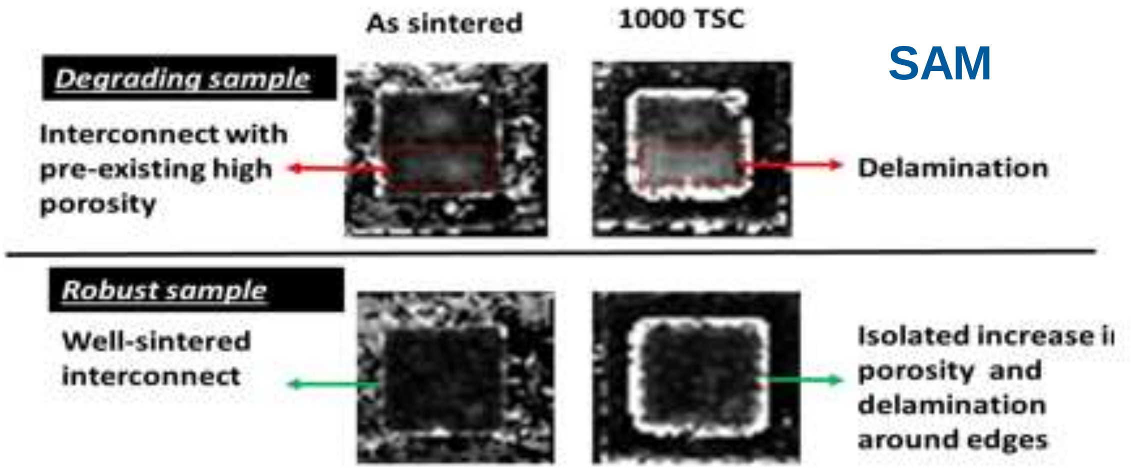
Where do we stand compared to commercial micro scale Ag sinter pastes?

Parameters	**Cu sintering**	**Ag sintering (commercial micro scales flakes based sinter paste)**
Temperature (°C)	250-275	230-280
Bonding pressure (MPa)	5-20	10-30
Sintering time (min)	1-5	1-5
Shear strength (MPa)	30-120	30-75
Sintering atmosphere	Nitrogen/Open bond chamber	Air/Nitrogen
Metallization compatiblity	Cu, Ag, Au	(Cu), Ag, Au

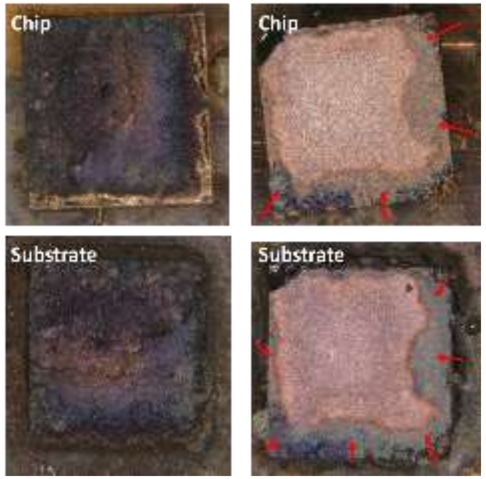
Reliability Under High Stress Condition

Copper Paste Development @ THI

SAM

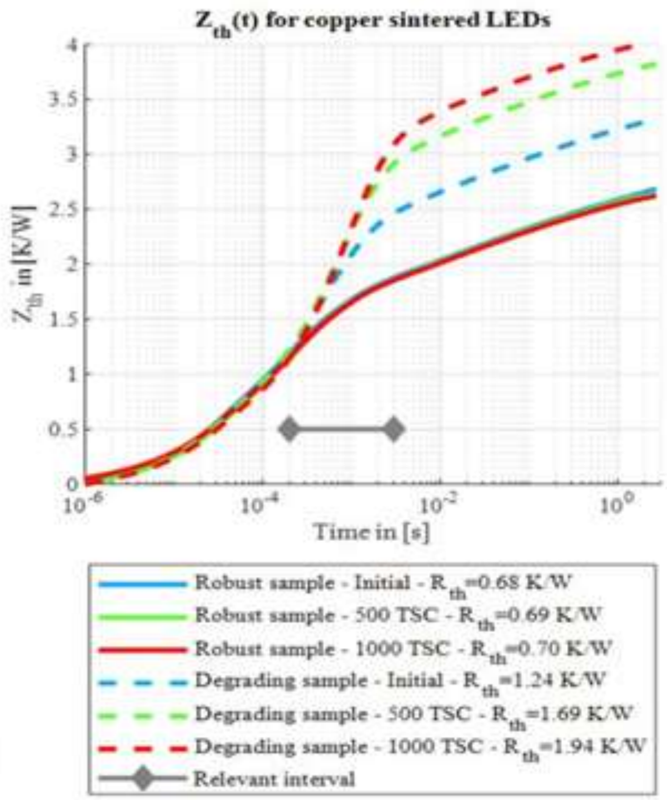


Oxidized interconnect



Oxidation is limited to outer edges due to low porosity of the interconnect

TTA

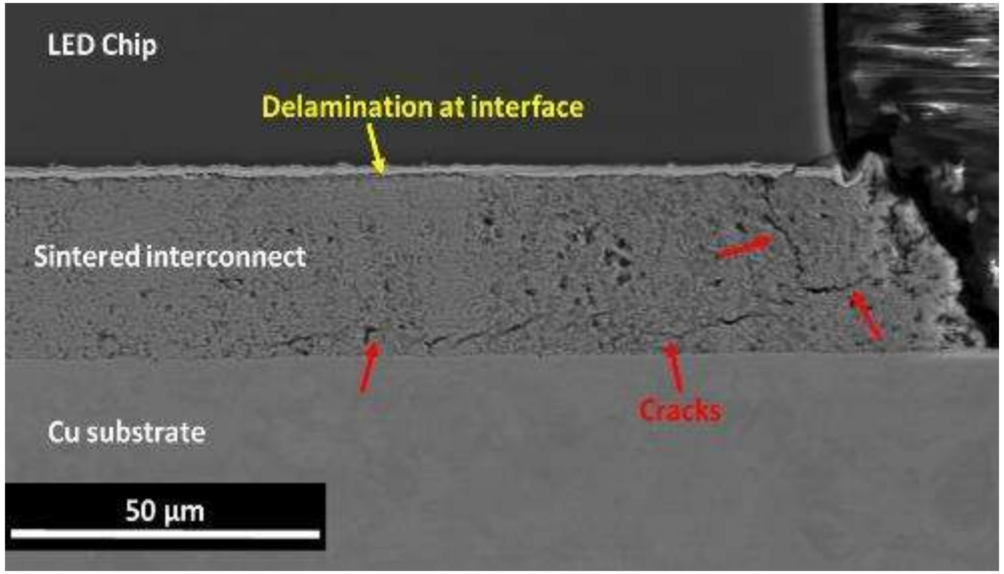


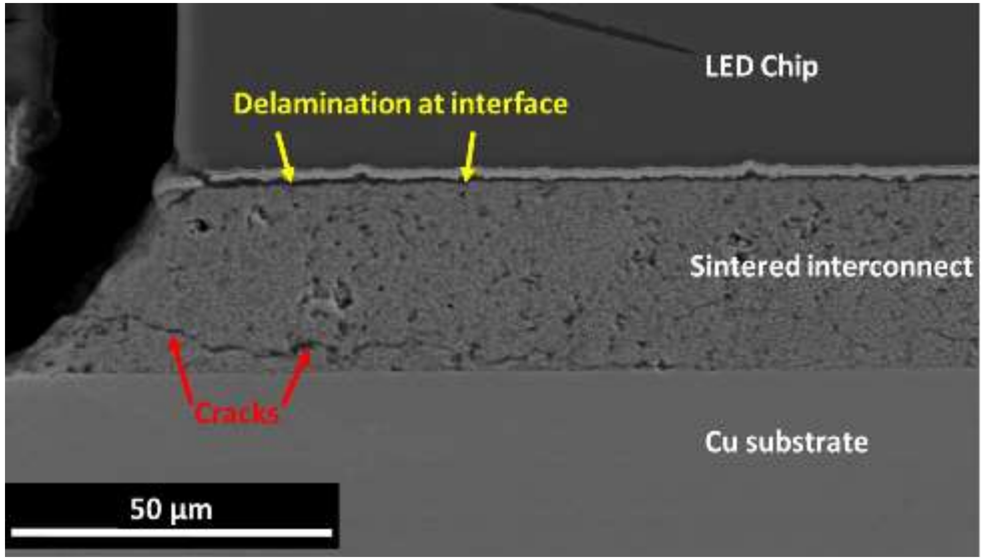
- **Measuring degradation by transient thermal impedance and Acoustic Microscopy (SAM)**

Crack Formation at the Corner

Copper Paste Development @ THI

- **1mm Silicon chip on copper (Power LEDs)**
- **1000 cycles, air-air – non-encapsulated - 40/125° C, 30min dwell time**
- **Crack formation and delamination at the corners observed**

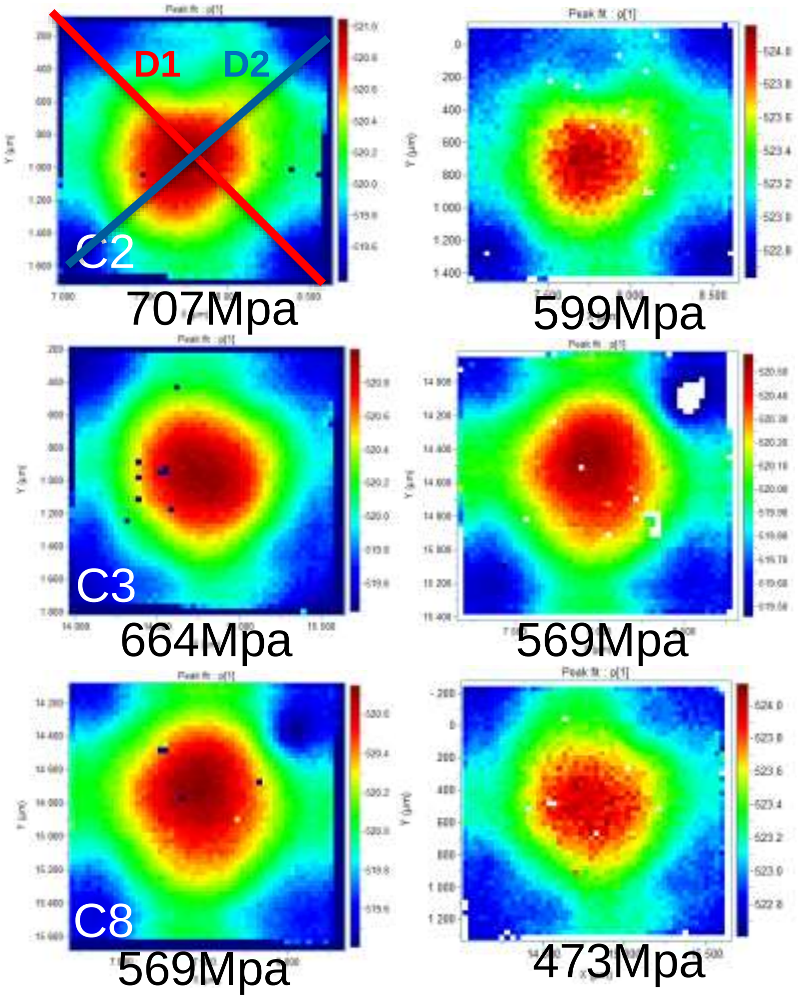




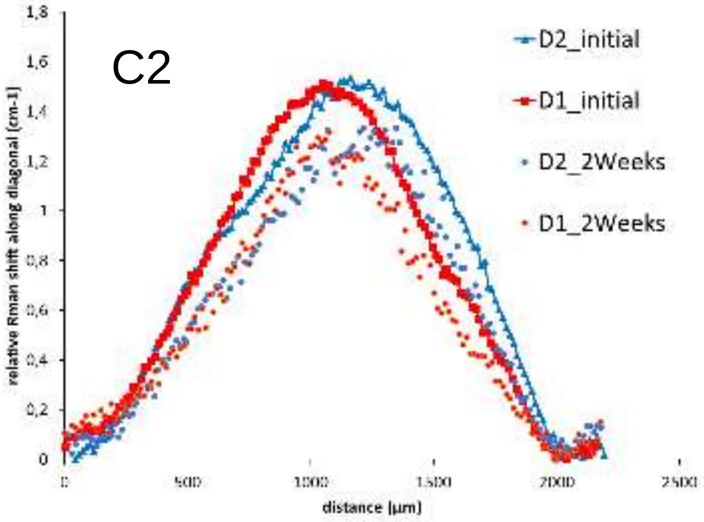
Stress detected by µ-RAMAN spectroscopy

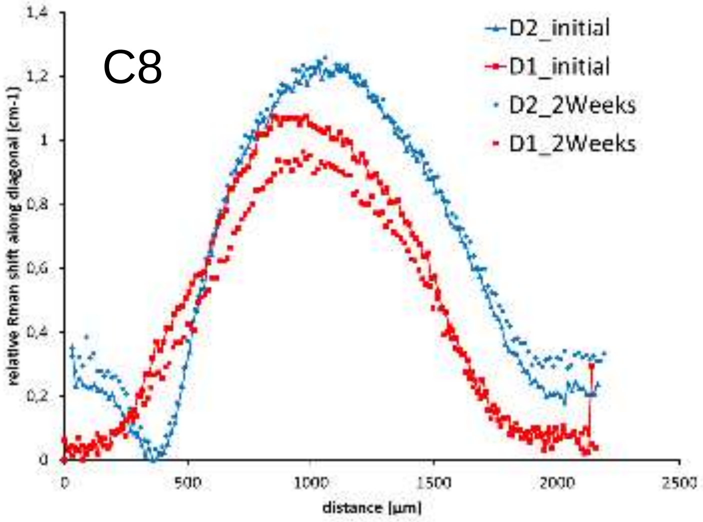
Copper Paste Development @ THI

after sintering 2 weeks after sintering



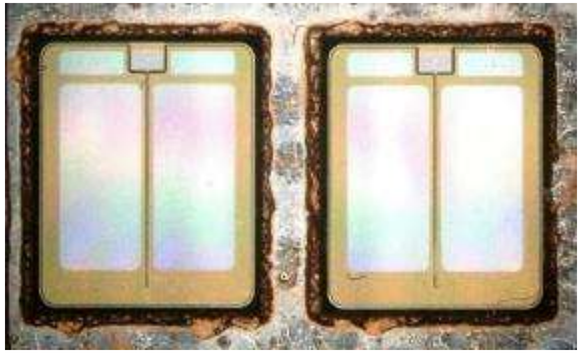
- **Silicon test chips (1.5mm x 1.5mm) sintered on copper plates with THI copper paste**
- **µ-RAMAN spectroscopy with 532 nm excitation wavelength**
- **Strain (stress) is measured by the RAMAN shift**
- **Secondary creep of copper interconnect can be measured**



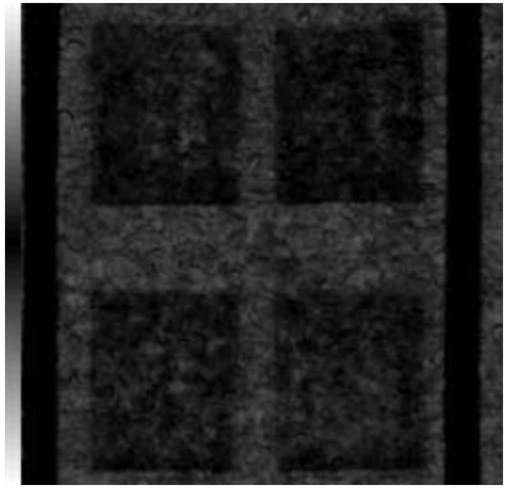


High Stress Thermal Shock MOSFET

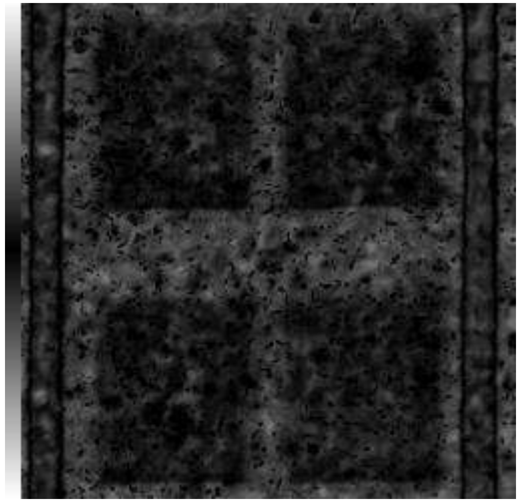
Copper Paste Development @ THI



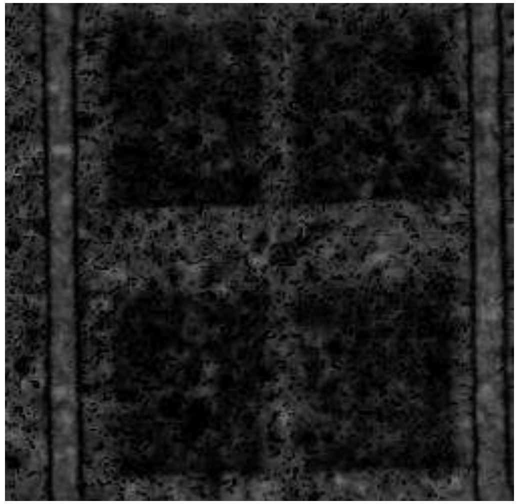
- **Air-Air – non-encapsulated - +175/-65° C, 30min dwell time**
- **No delamination observed by Scanning Acoustic Microscopy (SAM)**



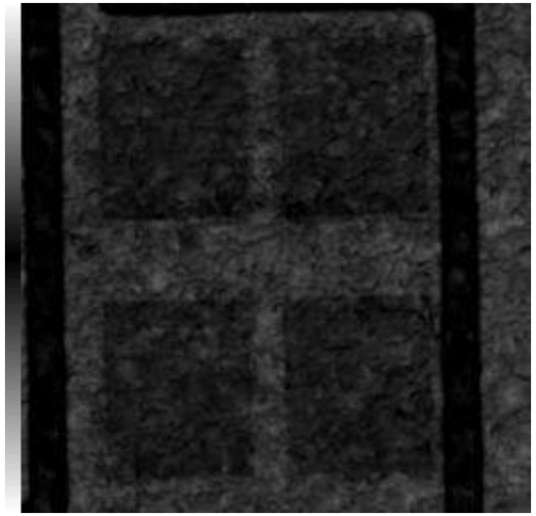
As sintered



500 cycles



1000 cycles

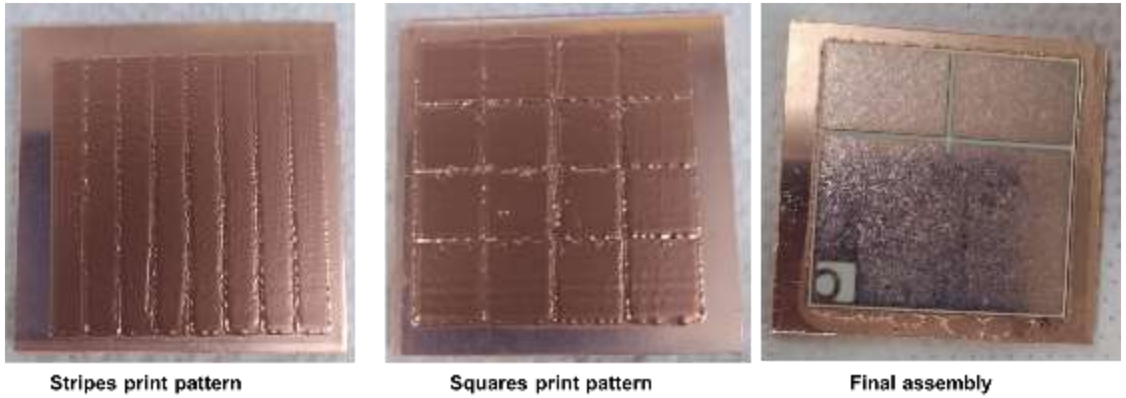


1500 cycles

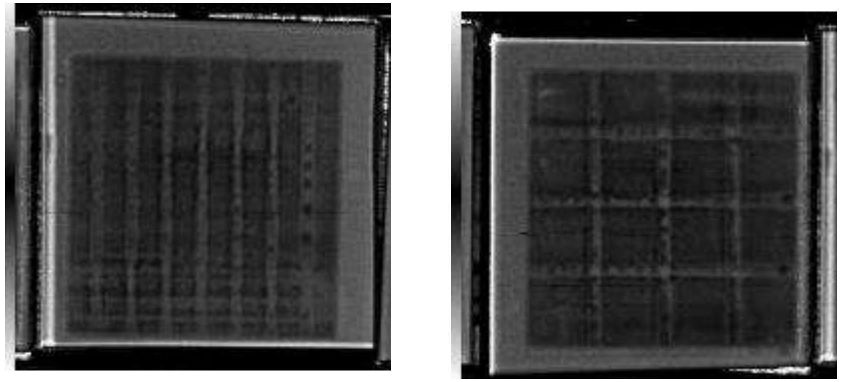
Large Area Bonding evaluation with NREL USA

Copper Paste Development @ THI

AMB with Cu metallization (1600mm² footprint) directly onto Cu baseplates



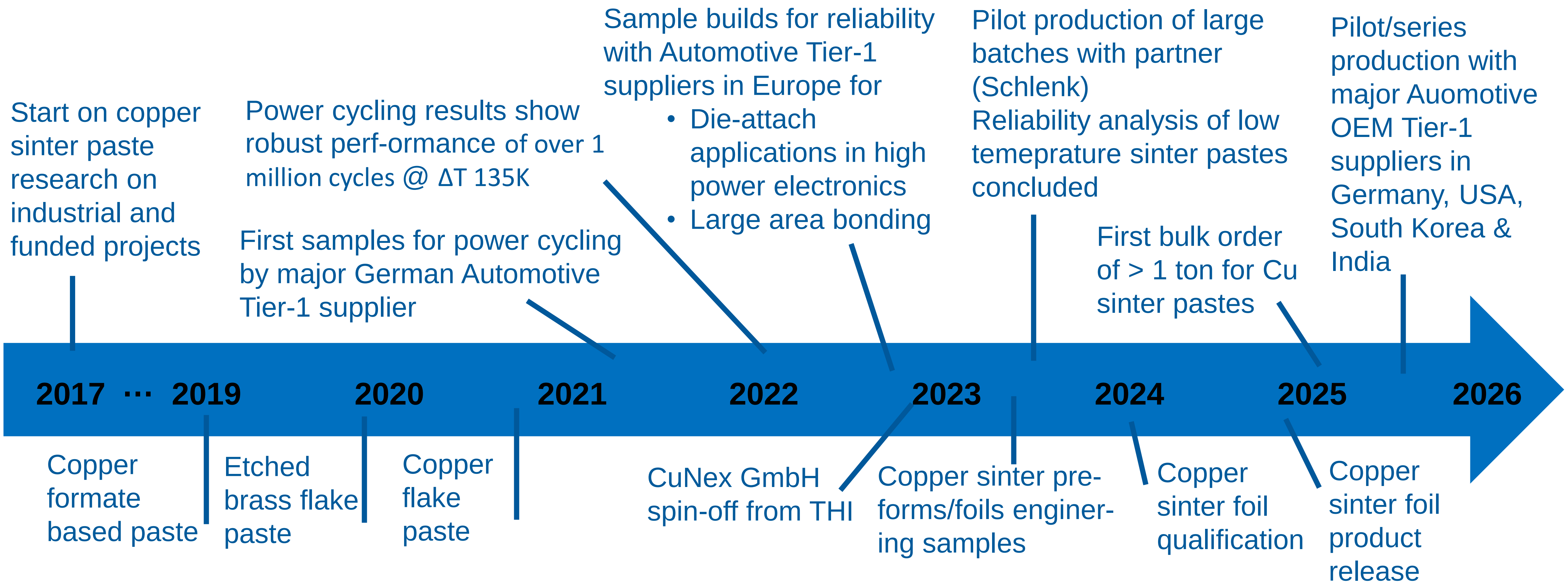
Budatec SP300
sinter press



- **SAM scans of the large area bonding show uniform sintering. No large voids/high porosity.**
- **Pre-drying – 15min in nitrogen @ 100° C**
- **Sintering – 5 min @ 275° C under nitrogen and 20 MPa bonding pressure**

Conclusion – History – Roadmap

Copper Paste Development @ THI



Start on copper sinter paste research on industrial and funded projects

Power cycling results show robust perf-ormance of over 1 million cycles @ ΔT 135K

First samples for power cycling by major German Automotive Tier-1 supplier

Sample builds for reliability with Automotive Tier-1 suppliers in Europe for
- Die-attach applications in high power electronics
- Large area bonding

Pilot production of large batches with partner (Schlenk)
Reliability analysis of low temeprature sinter pastes concluded

First bulk order of > 1 ton for Cu sinter pastes

Pilot/series production with major Auomotive OEM Tier-1 suppliers in Germany, USA, South Korea & India

Copper formate based paste

Etched brass flake paste

Copper flake paste

CuNex GmbH spin-off from THI

Copper sinter pre-forms/foils engineering samples

Copper sinter foil qualification

Copper sinter foil product release

PrLoMa – particel enforst loders and copper sintring

IQLED – low tmpratur copper sintering

ADDIRA – Cu conductive inks & pastes for ADAS applications

MaWisKI – AI based prediction of material properties & performance

DFG – Cu sinter paste

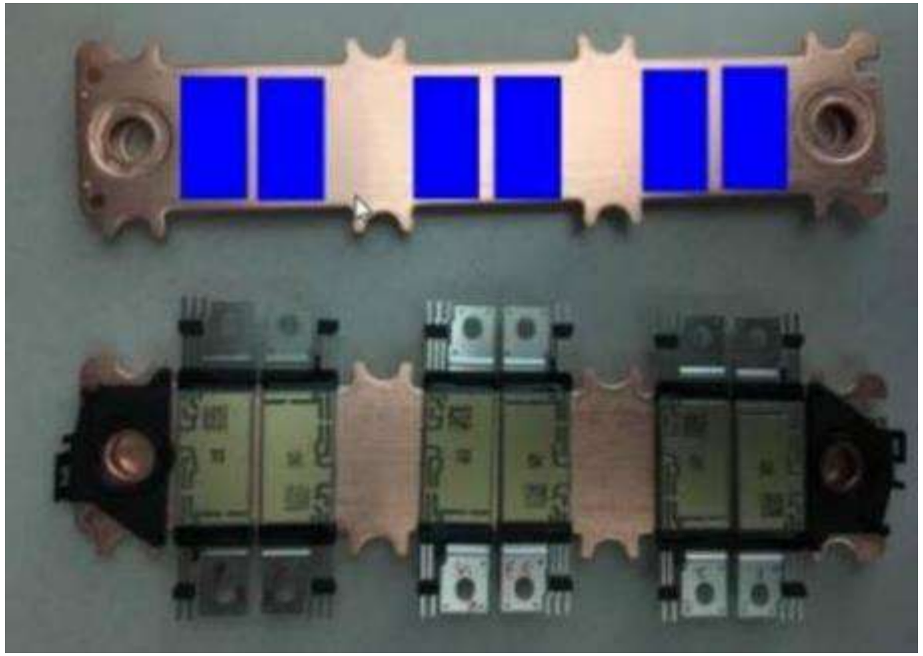
Copperfield – hybrid Cu sinter paste

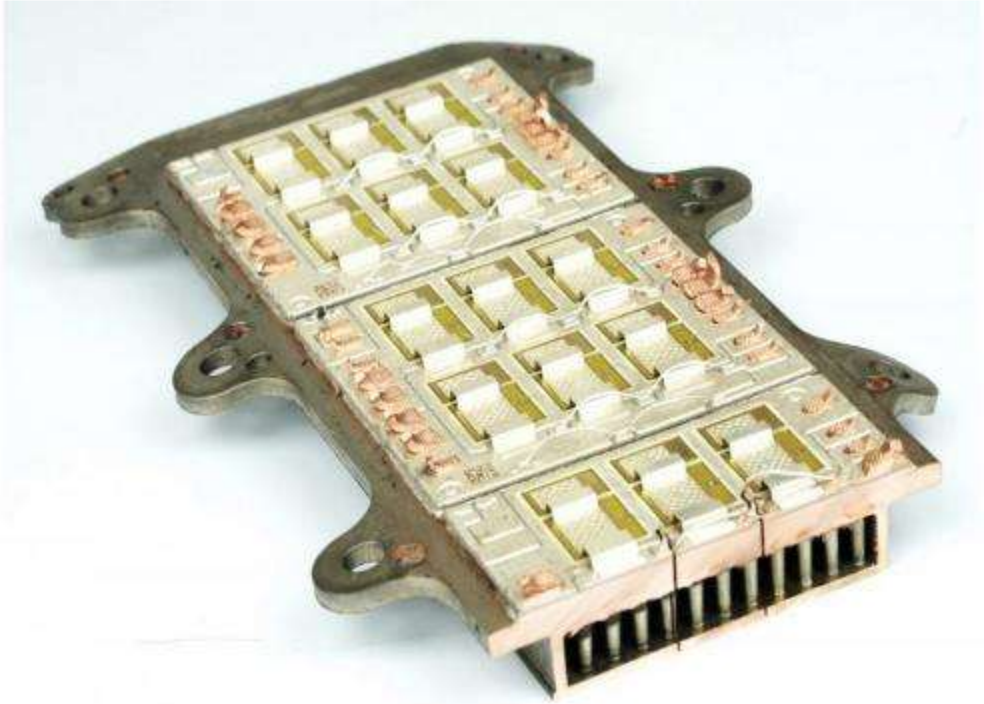
CuNex: Activated Copper Foil

JoinCuNext – Coated flakes

Thanks for your attention

Contact: Gordon.elger@thi.de





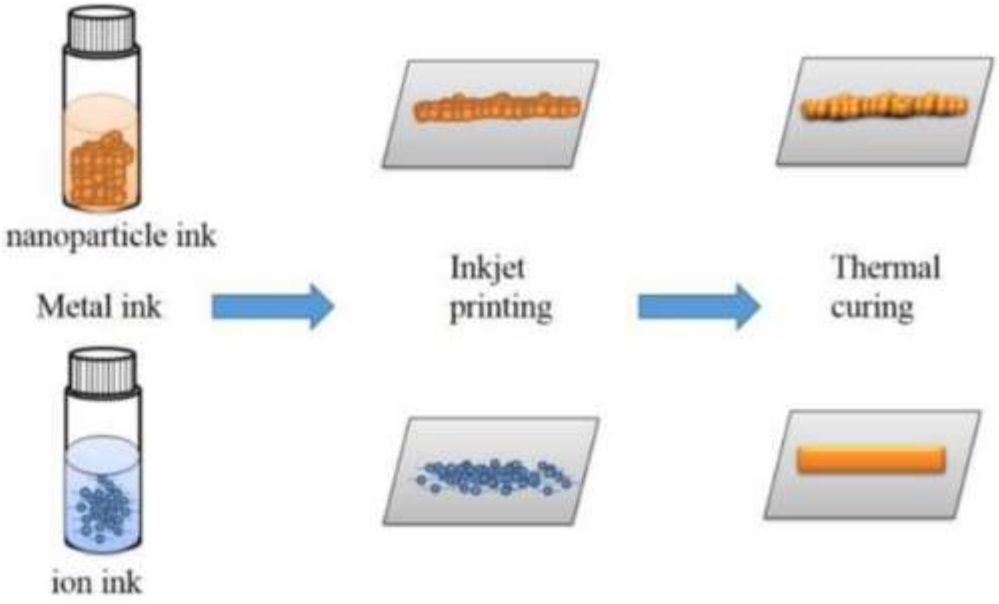
Motivation

Inks for Printed Electronics

- **Driven by organic flexible substrates with low degradation temperature**
  - metallization process at low temperature
  - use of metal nanoparticle, metal organic complexes (usually Ag, Au but also Cu)
- **Copper Nanoparticle inks**
- **Metal-organic decomposition inks, e.g. copper formiate**

$$Cu(HCOO)_{2(s)} \overset{heat}{\rightarrow} Cu_{(s)} + 2CO_{2(g)} + H_{2(g)}$$

$$Cu(HCOO)_{2(s)} \overset{heat}{\rightarrow} Cu_{(s)} + CO_{2(g)} + CO_{(g)} + H_2O_{(g)}$$

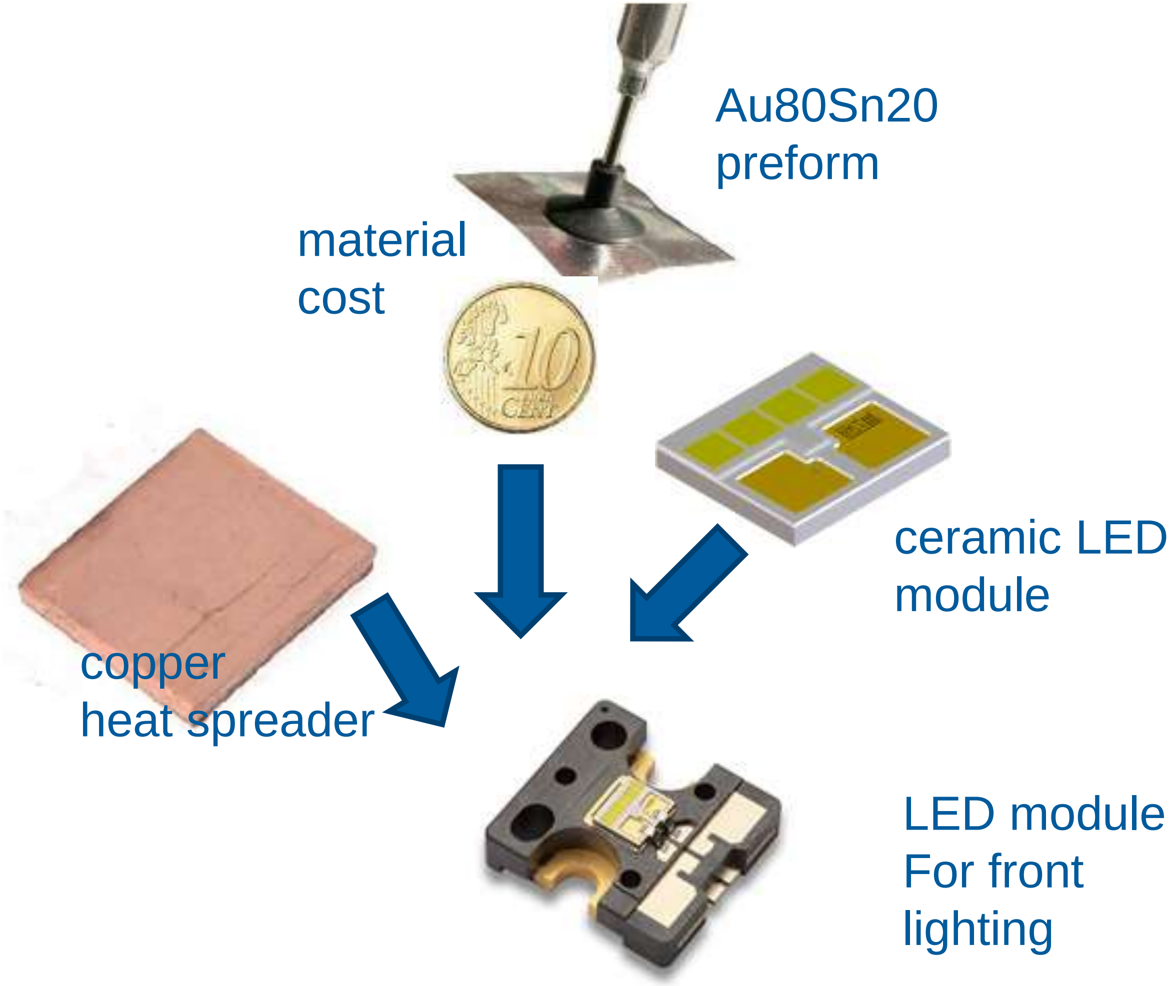


In dependence of binder/solvent temperature of decomposition 150°C ↔ 250°C

Motivation

Replacement of expensive AuSn

- **For heat management ceramic carrier is mounted on copper heat spreader**
- **Due to thermomechanical mismatch of copper and ceramic large thermomechanical stress**
- **AuSn used as solder with high fatigue resistance (yield strength 200MPa)**
- **Replacing AuSn solder by copper paste**
- **Process requirement:**
  - Temperature < 320^{o}C
  - Time < 30s



Au80Sn20 preform

material cost

ceramic LED module

copper heat spreader

LED module For front lighting

Motivation

Benefits of Copper Sintering

- **Pure Copper Interconnect**
- **Lower electro migration compared to silver**
- **Potentially low cost material**
- **Different application with different requirements**
  - High stress application, e.g. AuSn replacement (shear strength 100MPa)
  - Low stress application, e.g. replacement of high lead containing solder (shear strength roughly 20MPa)
  - High temperature application
  - Interconnect formation at low temperature with high temperature working condition
    - Application: low stress assembly, integration of components on organic substrates

Copper Sintering: Nanostructured Copper Flakes

General Concept of Surface Activation

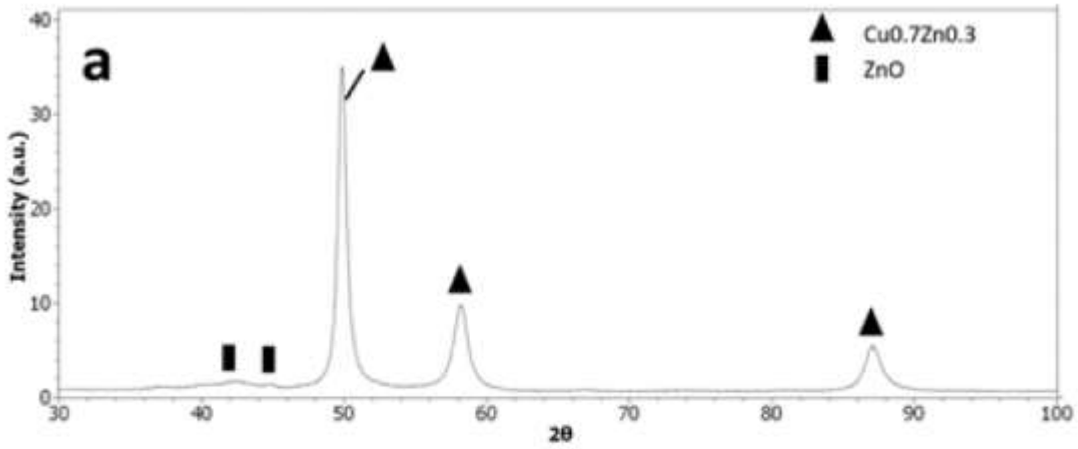
- **From a thermodynamic point of view sinter bonding is driven by temperature and surface energy reduction.**
- **For copper, sintering at 275°C the homologous temperature is with roughly 0.4 relatively low**
- **Important driving force comes from the high surface energy and curved surface inherent to a powder.**
  - Small particles have more surface energy and sinter faster than large particles.
- **The initial stage of sintering corresponds to neck growth between contacting particles**
  - Curvature gradients normally dictate the sintering behavior.
- **The intermediate stage corresponds to pore rounding and the onset of grain growth.**
  - During the intermediate stage the pores remain interconnected
- **Final stage sintering occurs when the pores collapse into closed spheres, giving a reduced impediment to grain growth.**
  - Usually the final stage of sintering starts when the component is more than 92% dense.
- **During all three stages, atoms move by several transport mechanisms to create the microstructure changes, including surface diffusion and grain boundary diffusion.**
- **Sintering models include parameters such as particle size and surface area, temperature, time, initial density, pressure and atmosphere.**

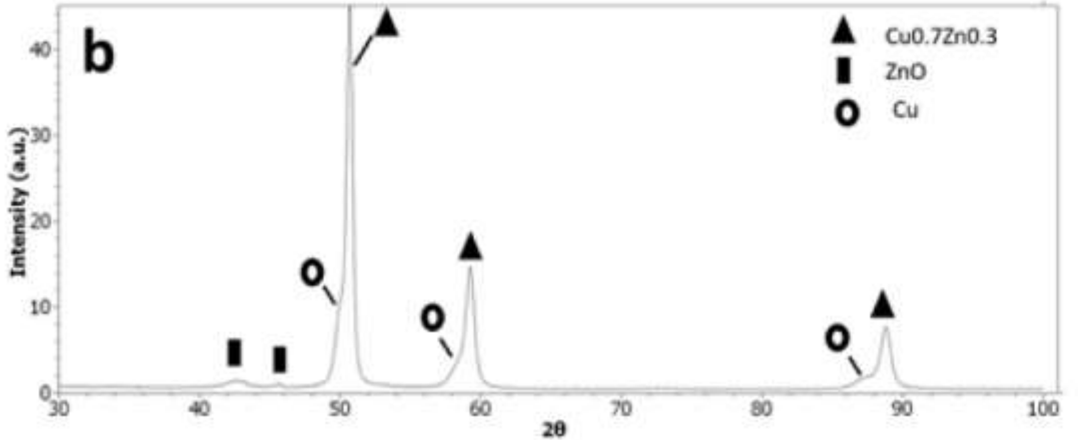
Copper Sintering: Nanostructured Copper Flakes

XRD befor and after etching

- For α-brass Zn is dissolved in the Cu chrystal, i.e. a solid solution with zinc atoms located at normal lattice sites
- The original brass powder shows the typical peak of Cu0.7Zn0.3n
- No Oxides are found in th original powder because its protected by 1.5wt% of steric acid
- After etching partly pure Cu is observed

a) XRD before etching Cu30%Zn



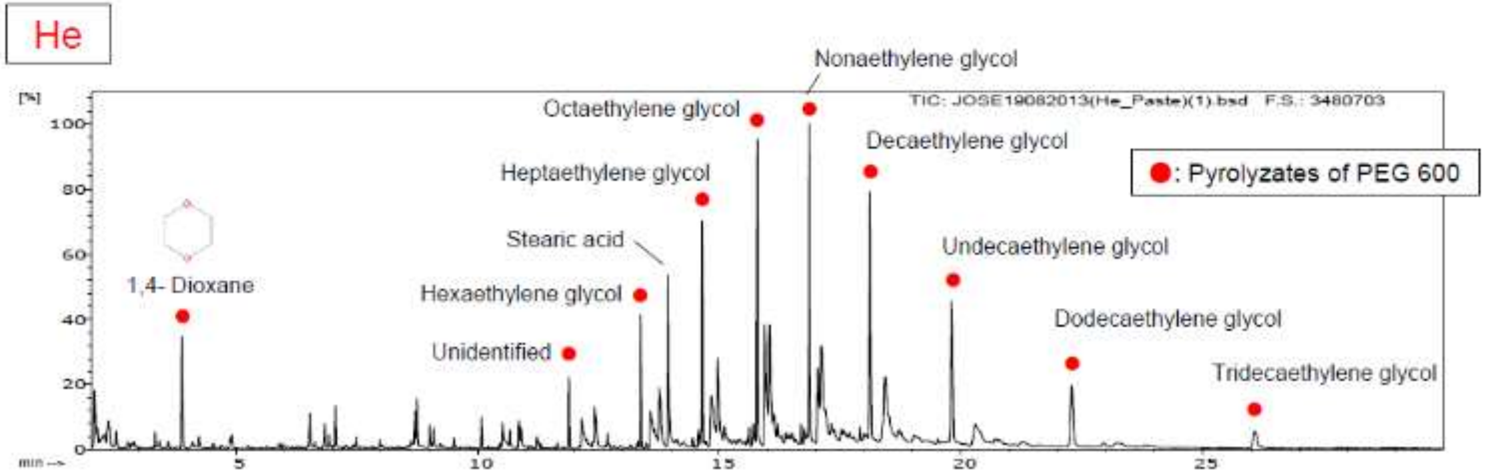


b) XRD after etching Cu30%Zn

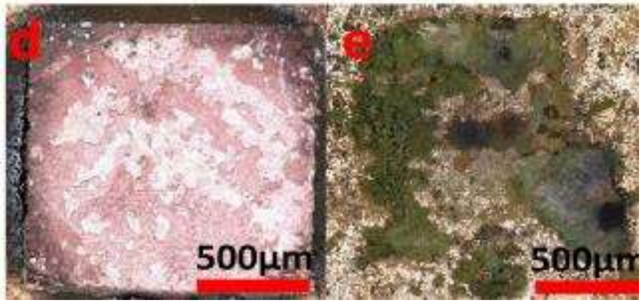
Copper Sintering: Nanostructured Copper Flakes

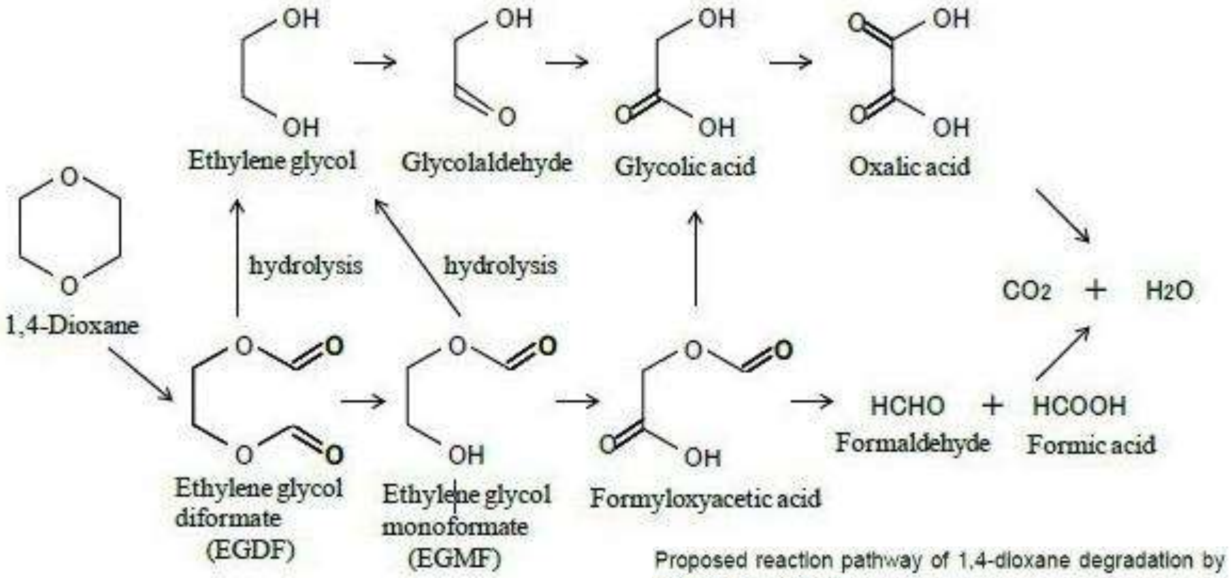
Reducing effects of the binder – possible phenomenon

- **Boiling temperature >250C**
- **Decomposition of PEG600 takes place above boiling point and depends from presence of oxygen**
- **Prevent agglomeration**
- **Reducing effect**



Sheared copper interface using (d PEG600 e) terpineol as binder



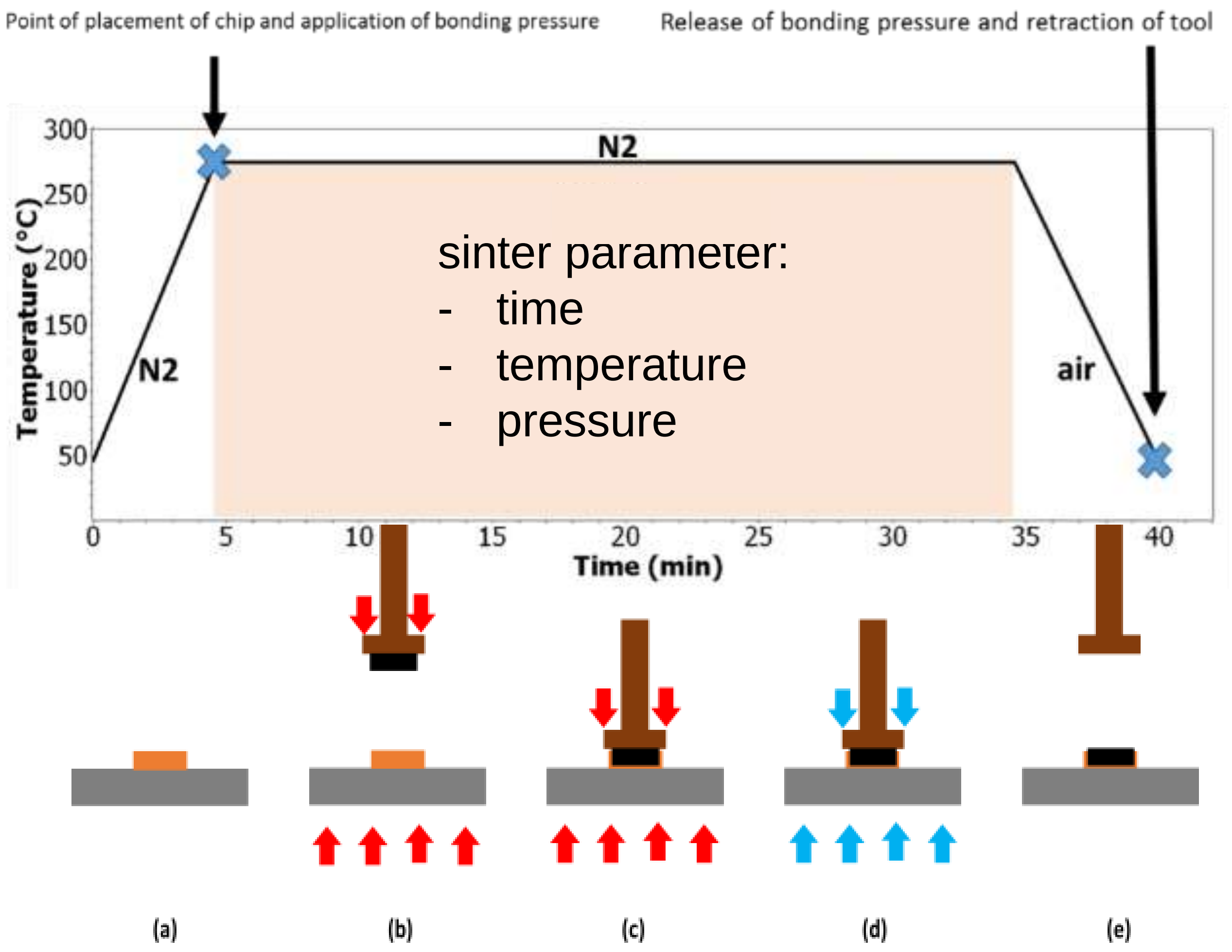


Proposed reaction pathway of 1,4-dioxane degradation by Maurio et al. (1997).

Copper Sintering: Nanostructured Copper Flakes

Sintering process & assembly

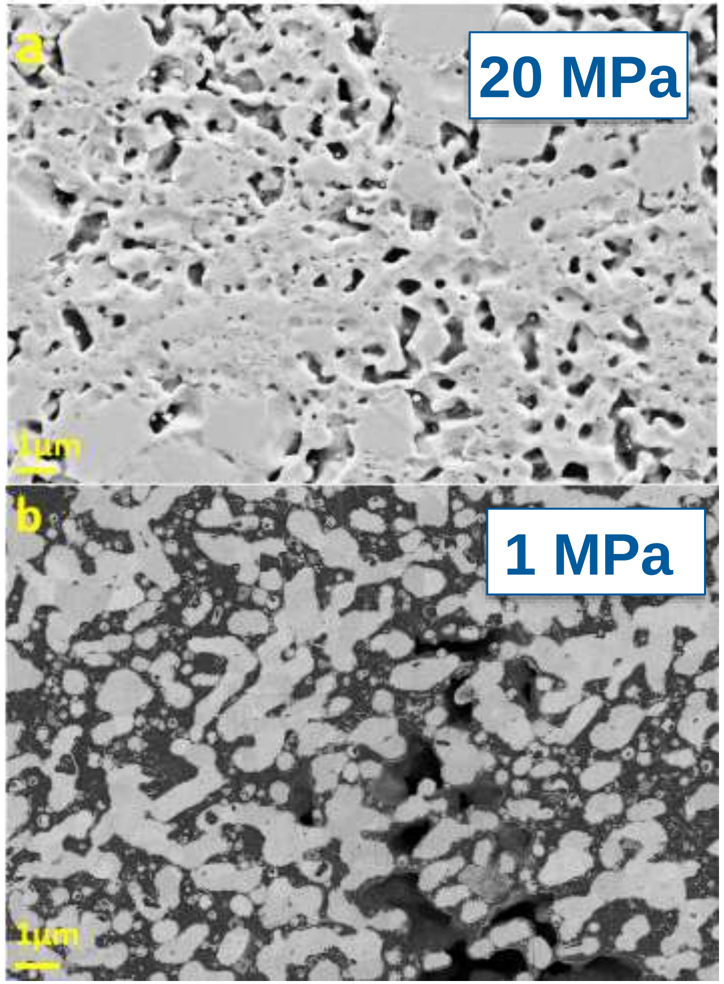
- 3,5 mm² Cu test chips and 100mm² substrates of 1mm thickness
  a) Stencil printing
  b) Ramp up to sintering temperature at 1K/s
  c) Place the chip once sintering temperature is reached.
  d) Bond with 20MPa pressure for 30min
  e) Release chip
- In production a press is used and process is performed on panel level



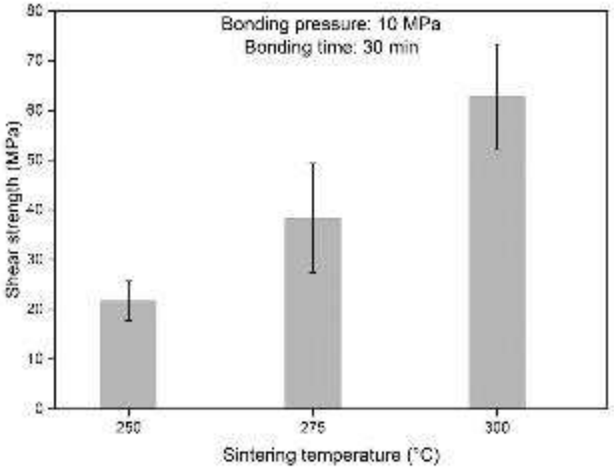
sinter parameter:
- time
- temperature
- pressure

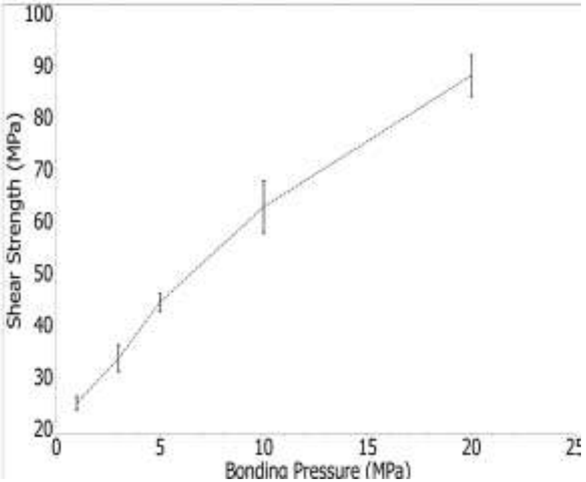
Copper Sintering: Nanostructured Copper Flakes

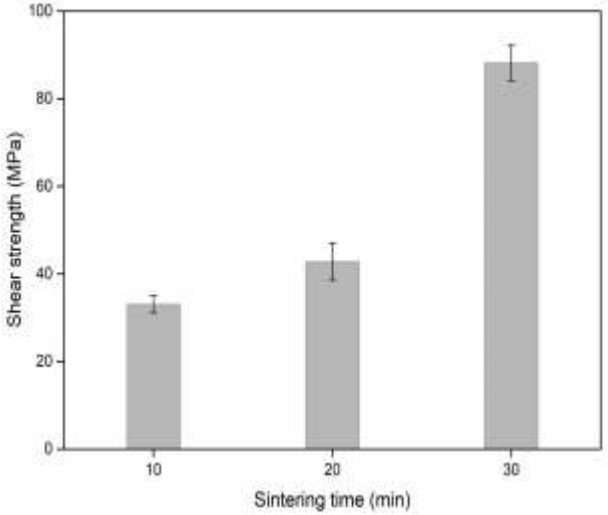
Results



- **Shear strength over 80MPa**
- **Expected parameter dependence**
- **Porosity depend on bond force**



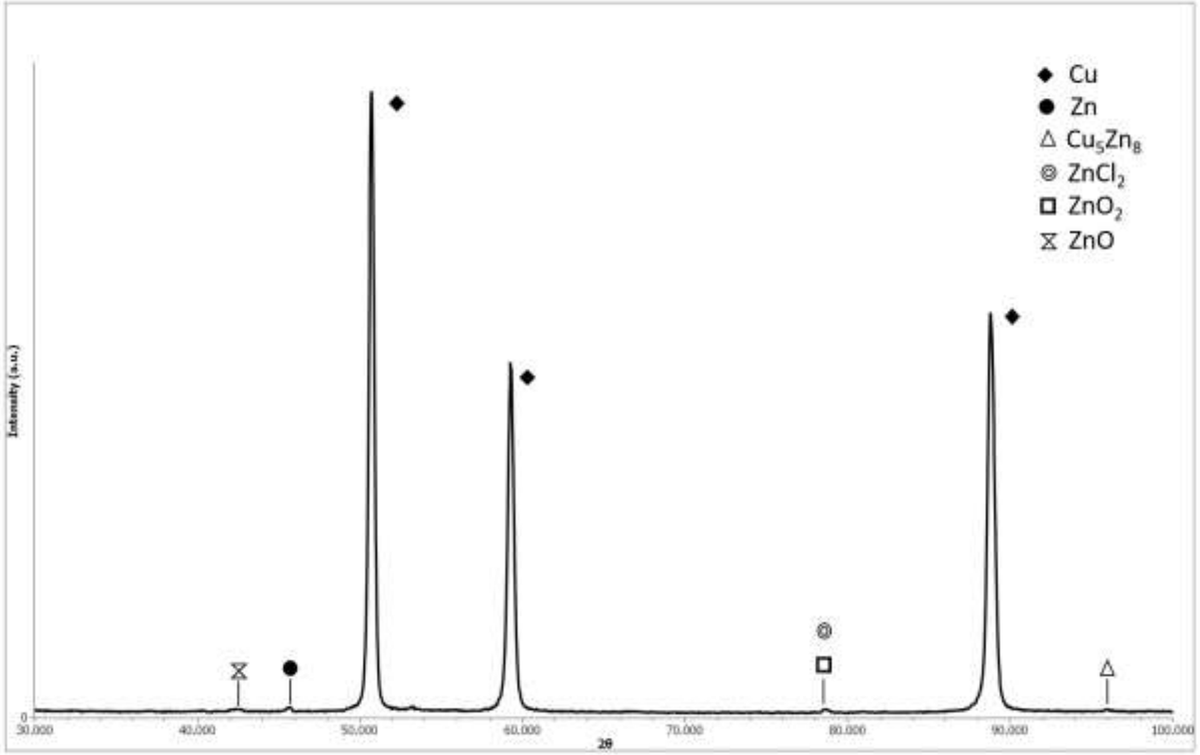




Copper Sintering: Nanostructured Copper Flakes

XRD on Sheared Interface

- **Risk of remaining Zn**
- **Risk of residual Cl**
- **Presence of Cu and Zn oxides**

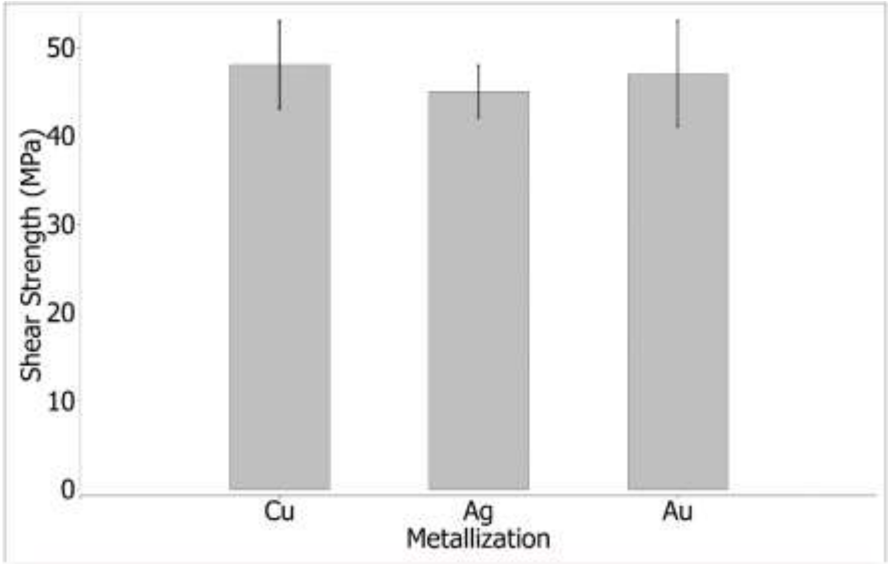


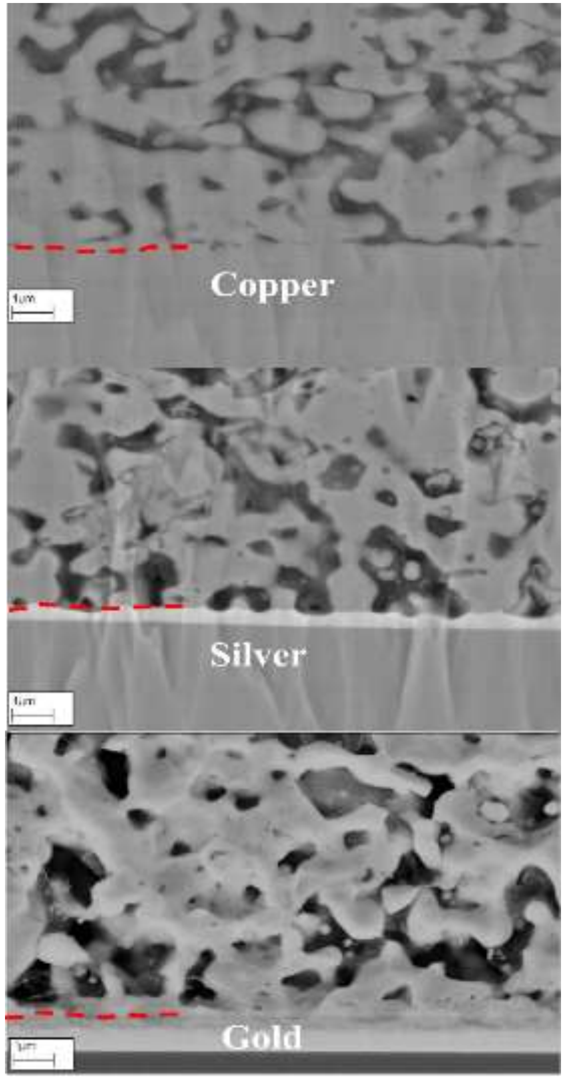
Copper Sintering: Nanostructured Copper Flakes

Compatibility with typical metallization

- **Impact of surface metallization on the shear strength of the sintered interconnect under bonding conditions of 5 MPa bonding pressure, 275^{o}C sinter temperature, 30 min sinter time and nitrogen atmosphere .**

- Copper
- Electroless NiAg
- Electroless NiAu





Copper Sintering: Nanostructured Copper Flakes

Densification

- **Results are in line with recent models**
  - Densification is a function of (Mackenzie-Shuttleworth model)

$$\frac{d\rho}{dt} = \frac{3}{2}\left(\frac{\gamma}{r} + P_{applied}\right)(1-\rho)\left(1 - \alpha\left(\frac{1}{\rho} - 1\right)^{\frac{1}{3}} ln\left(\frac{1}{1-\rho}\right)\right) 1/\eta$$

(sintering pressure P_{applied}, surface energy γ, particle radius r, geometrical constant α, density ρ, and densification viscosity η)

  - Pore mobility

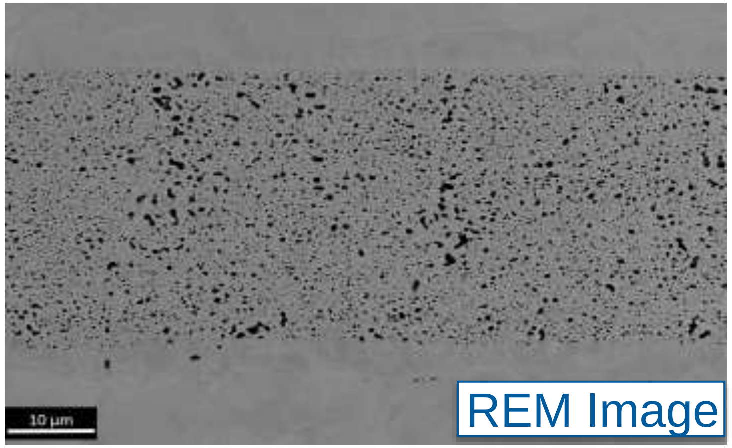
$$M_p^s = \frac{D_s \delta_s \Omega}{\pi r^4 kT}$$

(Ω: atom volume, δ_s: thickness of the surface through which diffusion occurs, r: pore radius, T: temperature, k: Bolzman constant, D_s: surface diffusion coefficient)

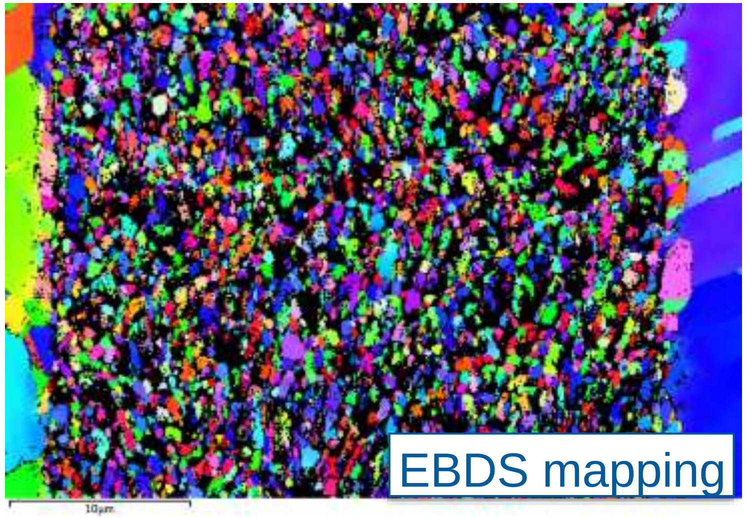
- **Decrease of pores in the final sintering stage**
- **With an assumption of circularity of the pores, the radius**

of the pore is calculated to be an average value of 0.05 µm. The average grain size calculated by EBSD is 0.6 µm.

5 MPa bonding pressure at 275 °C for 30 min



REM Image



EBDS mapping

Copper Sintering: Nanostructured Copper Flakes

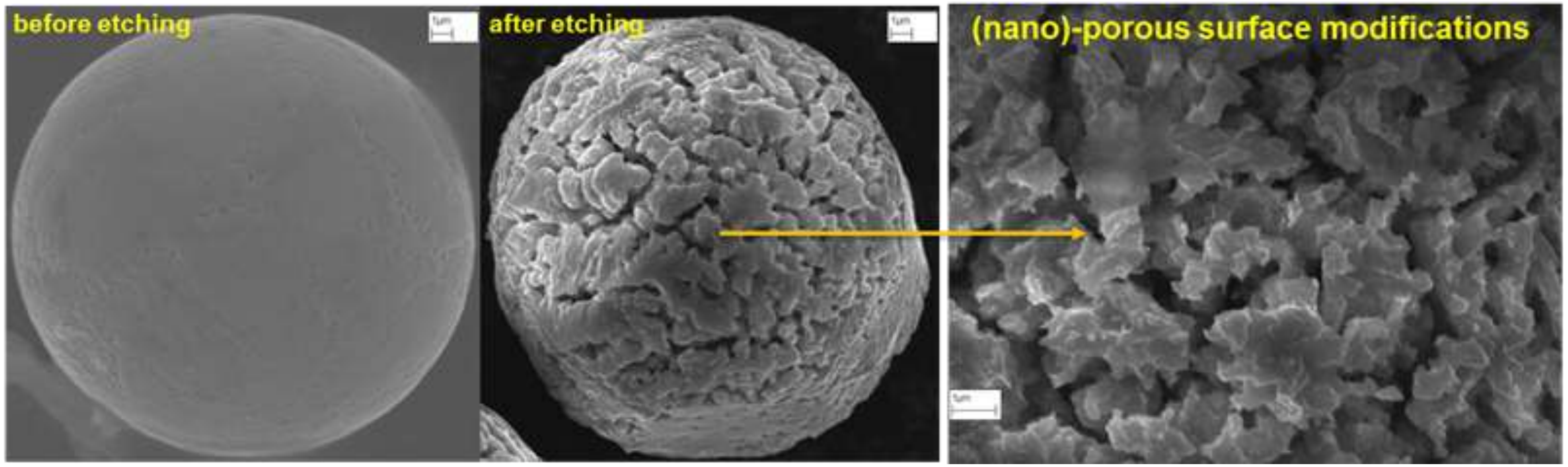
Brass and Bronze by Hydrochloric Acid

- **Nobel Cu remains and is separated from Sn or Zn**

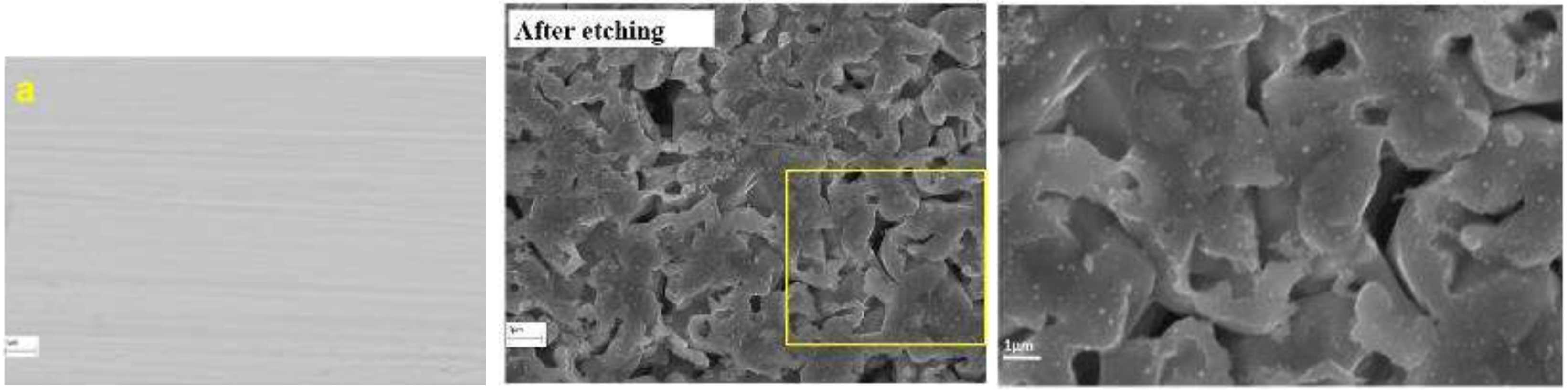
$$Sn(s) + 2HCl(l) \rightarrow SnCl_2(s) + H_2(g)$$

$$Zn(s) + 2HCl(l) \rightarrow ZnCl_2(s) + H_2(g)$$

- **Structured surface of 25µm bronze particle after echiching**



- **Structured surface of bronze substrate**



Copper Sintering: Nanostructured Copper Flakes

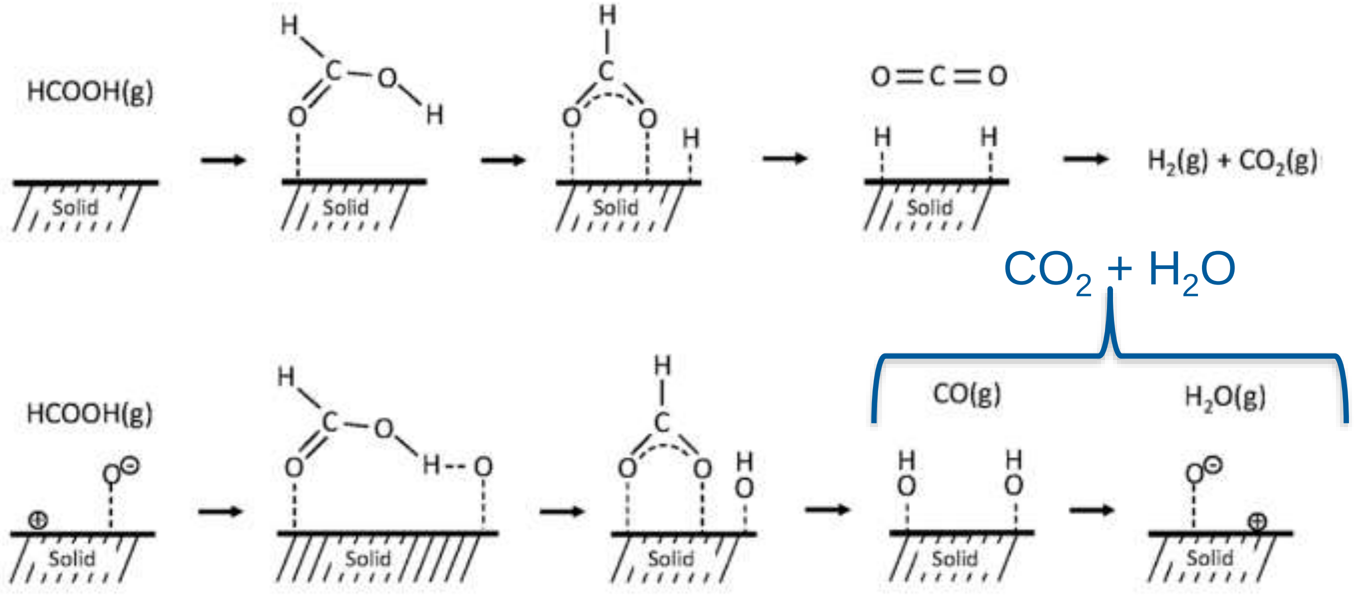
Compatibility with typical metallization

- **Control of porosity by pressure and time**
- **Higher Porosity**
  - reduces shear strength
  - increases elasticity, i.e. reduces E modulus)
- **Design of optimized interconnect for thermomechanical fatigue**

Copper Sintering: Copper Formiate Decomposition

Formiat Decomposition

- **Formic acid decomposition**
  - Dehydrogenization $HCOOH \rightarrow H_2 + CO_2$ ΔG^0= - 32.9 kJ/mol (Gl.1)
  - Dehydration $HCOOH \rightarrow H_2O + CO$ ΔG^0= - 20.7 kJ/mol (Gl.2)
- **Catalytic interaction with metal surfaces**



Pure metal

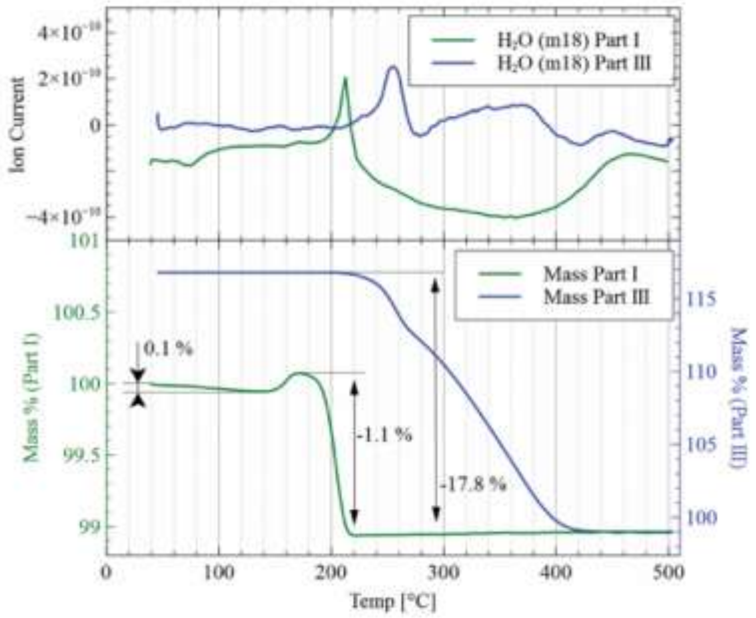
Metal oxide

$CO_2 + H_2O$

Copper Sintering: Copper Formiate Decomposition

Formiat Desorption and Sublimation – Camical Vapour Deposition

- **TGA of Copper under formic acid vapor**



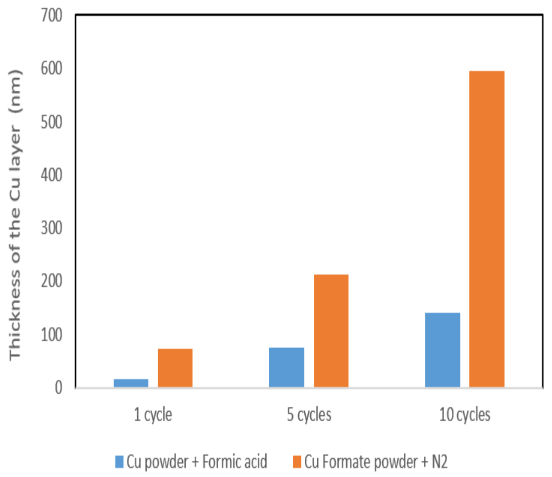
$$Cu(s) + 2\ HCOOH(g) \leftrightarrow Cu(COOH)_2(s) + H_2O(g)$$

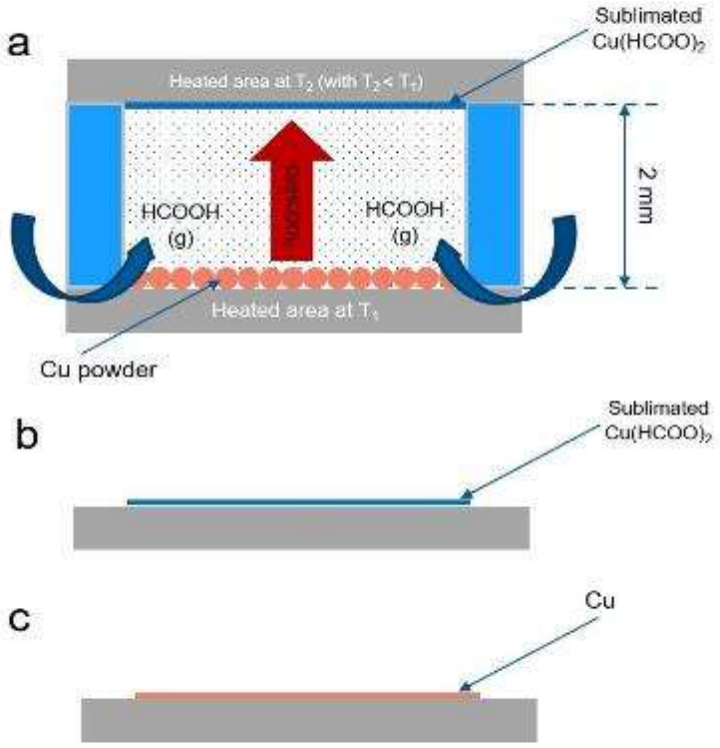
$$CuO(s) + 2\ HCOOH(g) \leftrightarrow Cu(COOH)_2(s) + H_2(g)$$

$$CuO_2(s) + 2\ HCOOH(g) \leftrightarrow Cu(COOH)_2(s) + H_2(g) + O_2(g)$$

- **Deposition/Sublimation of copper formate and decomposition to copper**

$$Cu(HCOO)_i(s) \leftrightarrow Cu(HCOO)_i(g)$$





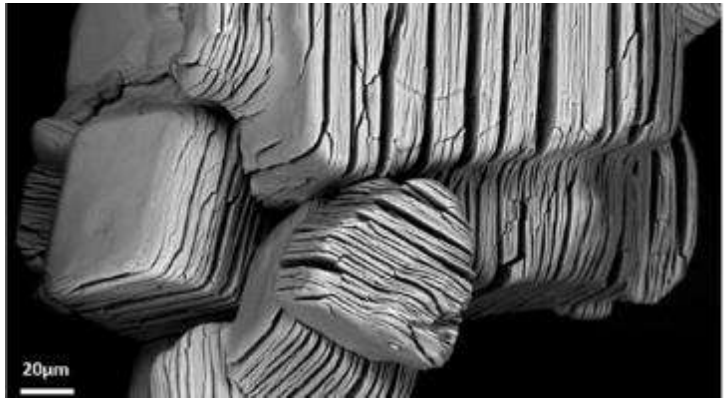
Copper Sintering: Copper Formiate Decomposition

Formiat Desorption and Sublimation – Camical Vapour Deposition

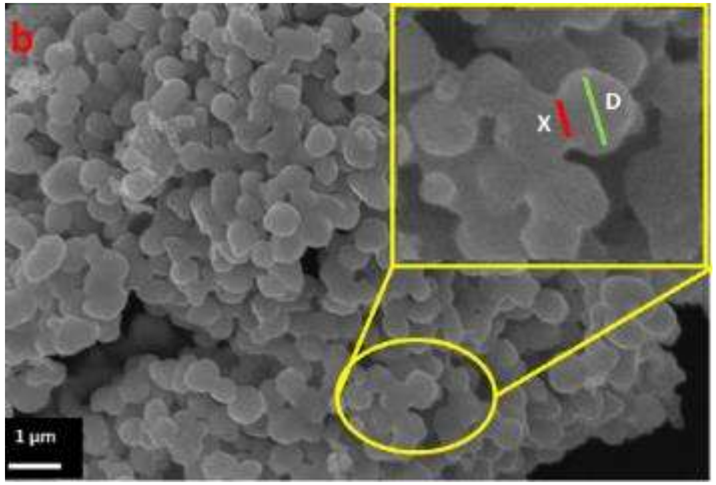
- **Commercial copper-2-formiate, grinded to 1µm particle**
- **Scaling model**
  - Sinter time t scales with particle size D

$$t_2/t_1 = (D_2/D_1)^n$$

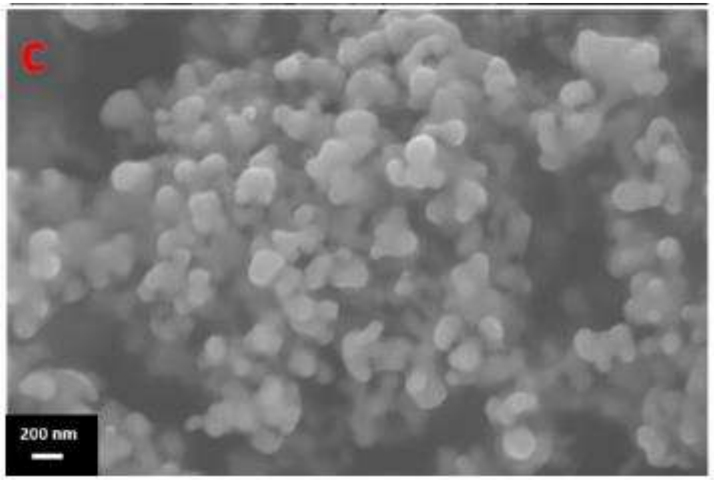
- **Binder depended copper particle diameter**
  - No binder 500nm
  - PEG500 200nm



Copper Formate before grinding



Decomposition, no binder

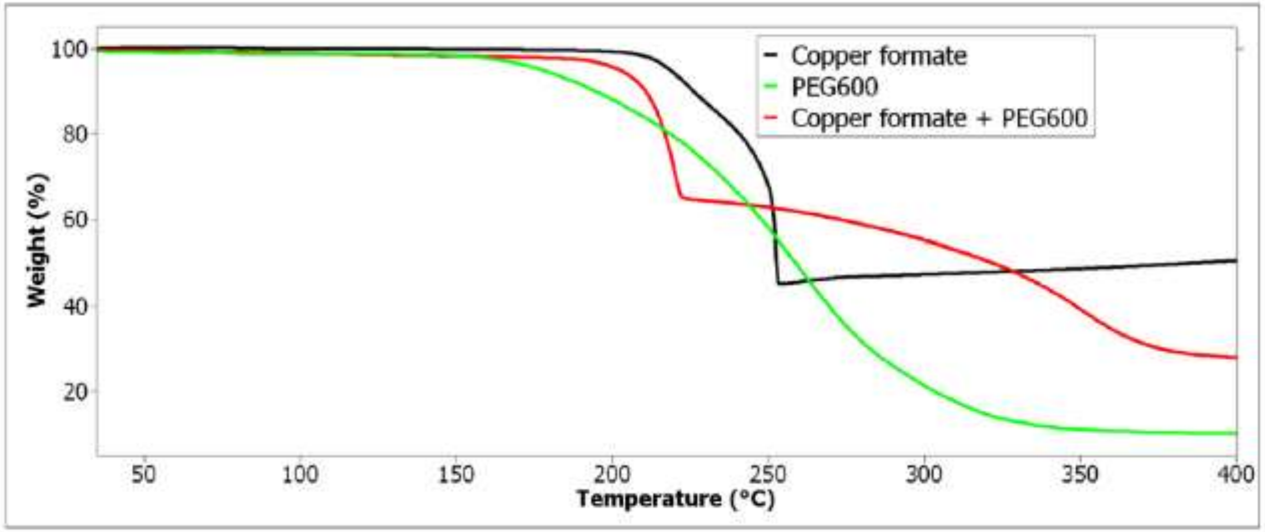


Decomposition in PEG600

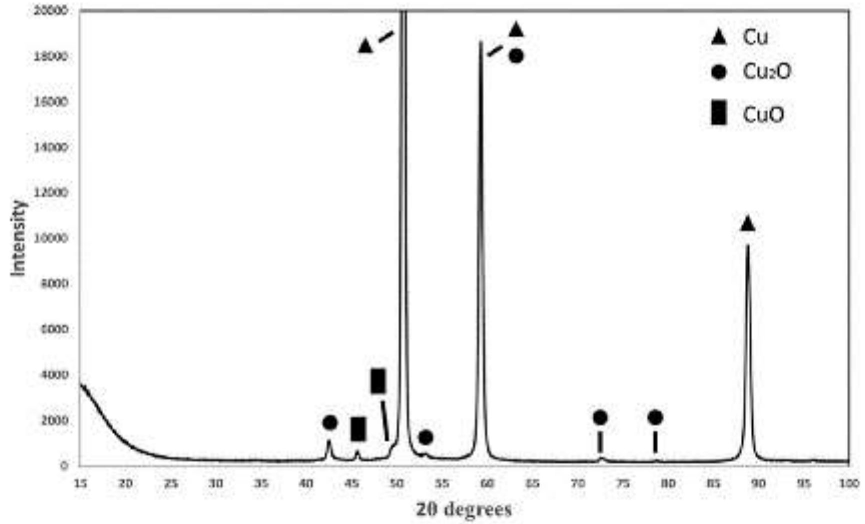
Copper Sintering: Copper Formiate Decomposition

Binder Dependent Decomposition Temperature

- **Decomposition temperature is reduced by 20°C by PEG600due to earlier volatilization of free carboxyl groups dissociated already at lower temperatures by the presence of PEG600.**
- **During decomposition under air small amount of oxide is formed, i.e. oxidation protection required**



TGA of dopper(II)formiate (no binder, PEG600, copper(II) formiate in PEG



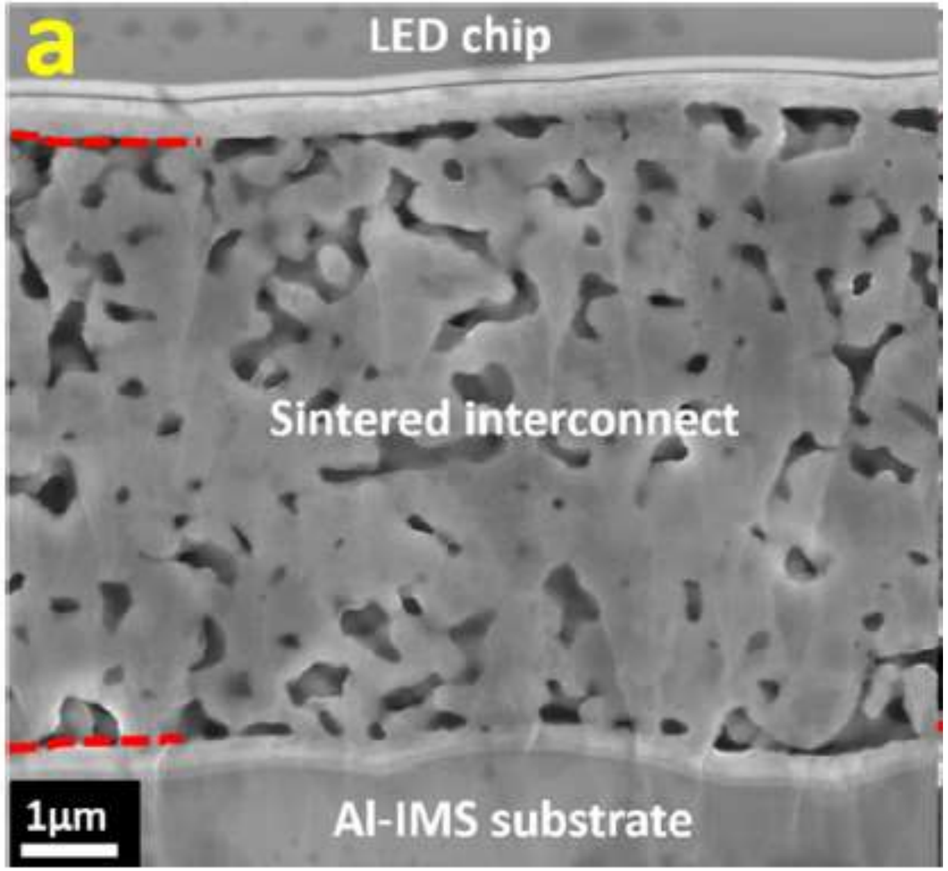
XRD analysis of the nanoparticles produced via thermal decomposition of the copper(II) formate. The pattern is recorded with the crystals under air, i.e. under 21%oxygen by volume.

Copper Sintering: Copper Formiate Decomposition

Interface and Shear valuues

- **Test sample: LED on Al-IMS**
- **Same process as with etched copper particles**
  - 275°C, 20MPa, 30min
- **Well sintered interconnect**

- **Function of binder: development of fine nano powder forming at low temperature**
- **Ongoing development of binder: inorganic binder as amino-2-propanol and amines like hexamine**
  - Reducing agent supporting the dissociation of carboxyl groups
  - Encapsulation of copper to reduce the grouwth

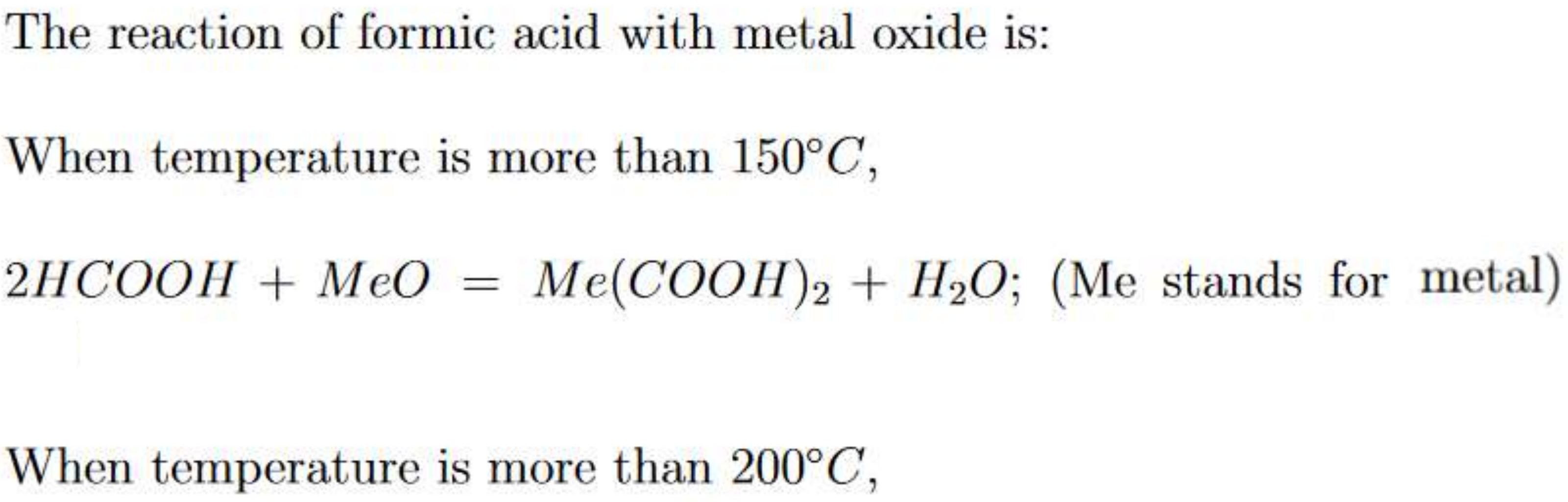


Conclusion

Formic Acid Decomposiotion

Common insufficient explanation

- **Very common, the interaction of formic acid with metalls is reported incorrectly, e.g.:**

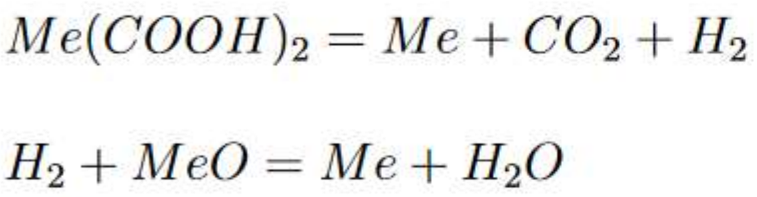


The reaction of formic acid with metal oxide is:

When temperature is more than 150°C,

$$2HCOOH + MeO = Me(COOH)_2 + H_2O;\ \text{(Me stands for metal)}$$

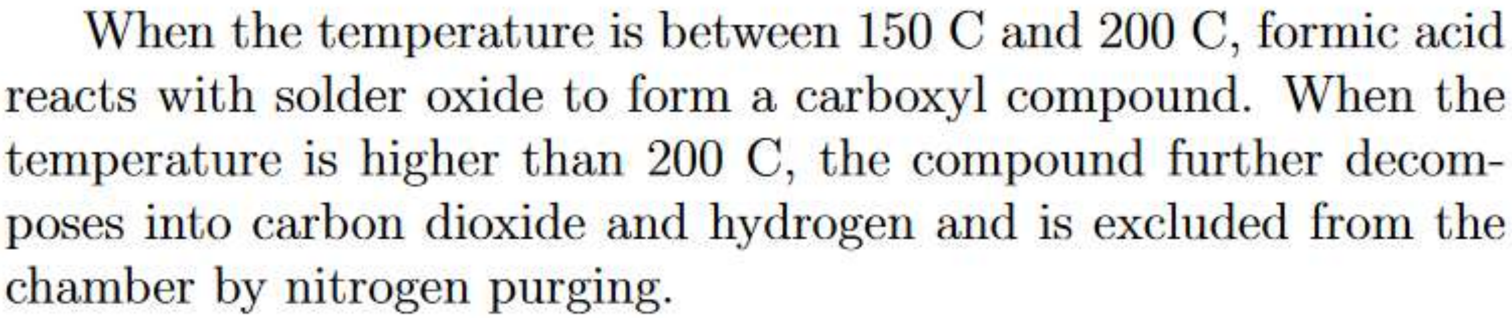
When temperature is more than 200°C,



$$Me(COOH)_2 = Me + CO_2 + H_2$$

$$H_2 + MeO = Me + H_2O$$

Study of Fluxless SolderingUsing Formic Acid Vapor
Wei Lin and Y. C. Lee, IEEE TRANSACTIONS ON ADVANCED PACKAGING, VOL. 22, NO. 4, NOVEMBER 1999



When the temperature is between 150 C and 200 C, formic acid reacts with solder oxide to form a carboxyl compound. When the temperature is higher than 200 C, the compound further decomposes into carbon dioxide and hydrogen and is excluded from the chamber by nitrogen purging.

International Journal of Pure and Applied Mathematic, Volume 118 No. 16 2018, 1433-144

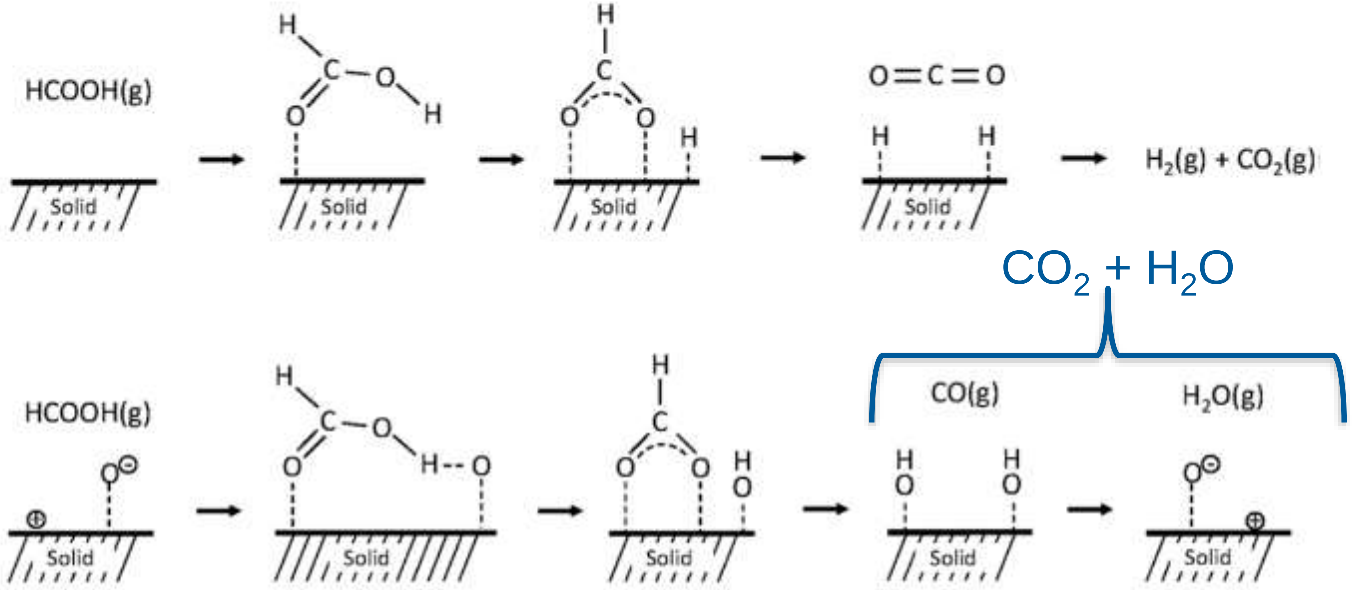
Formic Acid Decomposition

Formic acid self decomposition

- **Formic acid decomposition**
  - Dehydrogenization $HCOOH \rightarrow H_2 + CO_2$ ΔG^0= - 32.9 kJ/mol (Gl.1)
  - Dehydration $HCOOH \rightarrow H_2O + CO$ ΔG^0= - 20.7 kJ/mol (Gl.2)
- **Catalytic interaction with metal surfaces**

Pure metal

Metal oxide



$CO_2 + H_2O$

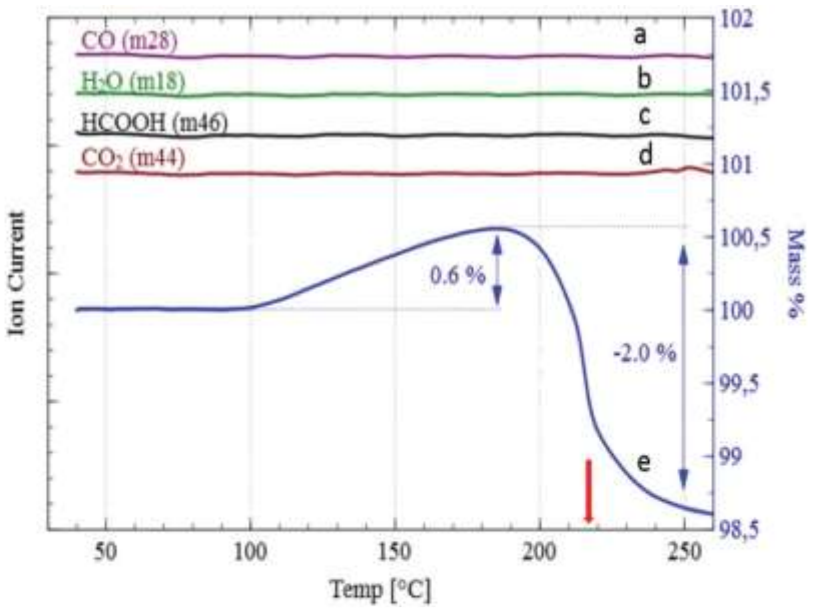
- **https://advanceseng.com/concept-progress-intelligent-spindles/**

Thermal Gravimetric Analysis

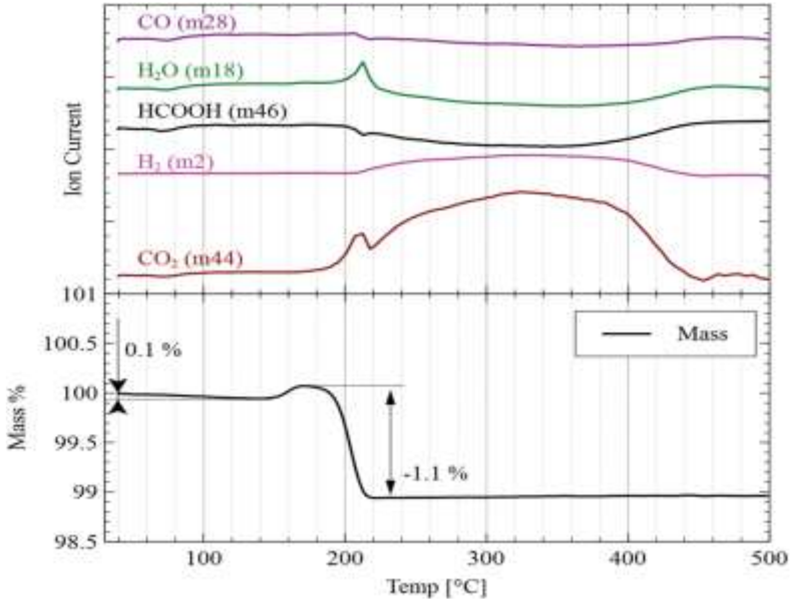
Oxidized Metal powder under formic acid

- **Thermal gravimetric analysis under formic acid with mass spectrometer for analysis of gaseous decomposition products**
- **SAC powder (type 5) and weakly oxidized copper powder (type 6)**

SAC (atimic mass Sn 118u)



Weakly oxidized Cu (atomic mass 63u)

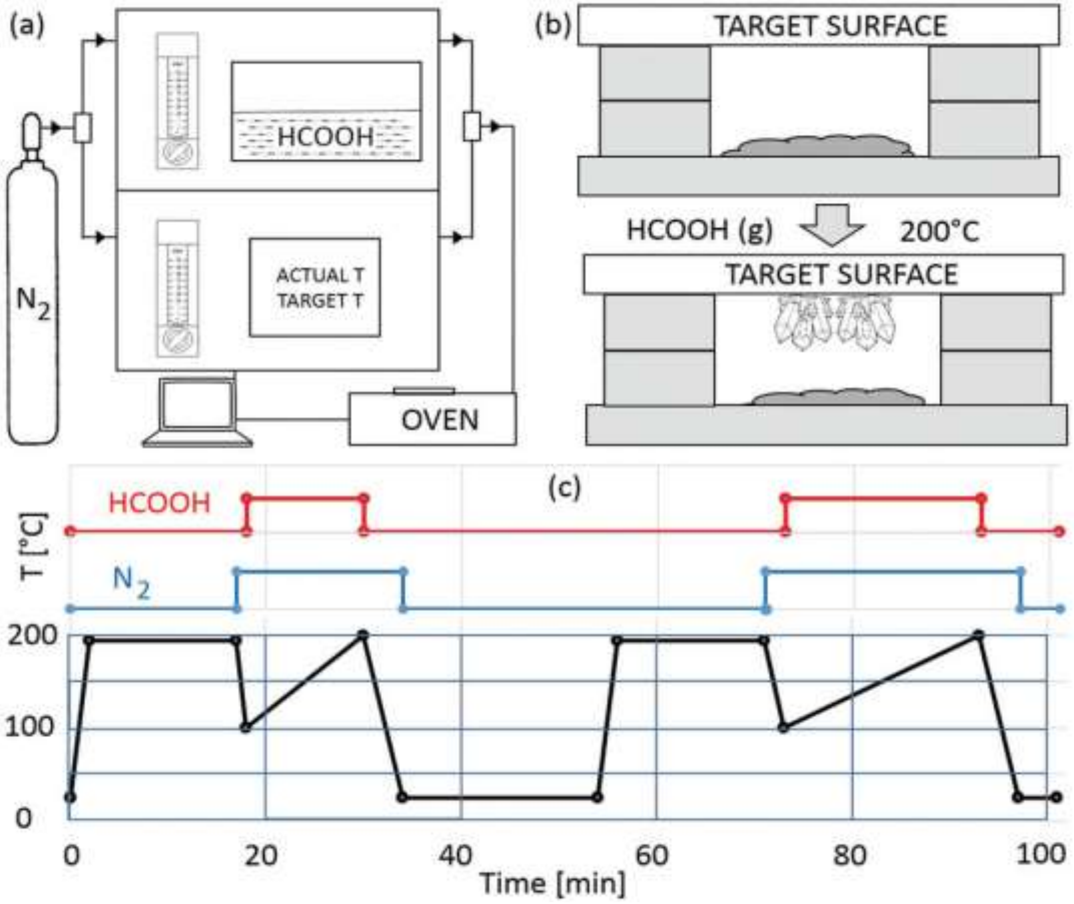


- **Mass reduction is too large to be explained by loss of oxygen**
- **CO_2 and H_2O peaks found for copper but not for SAC**

Metall Formiate Evaporation

Experimental setup to prove evaporation of metal formiate

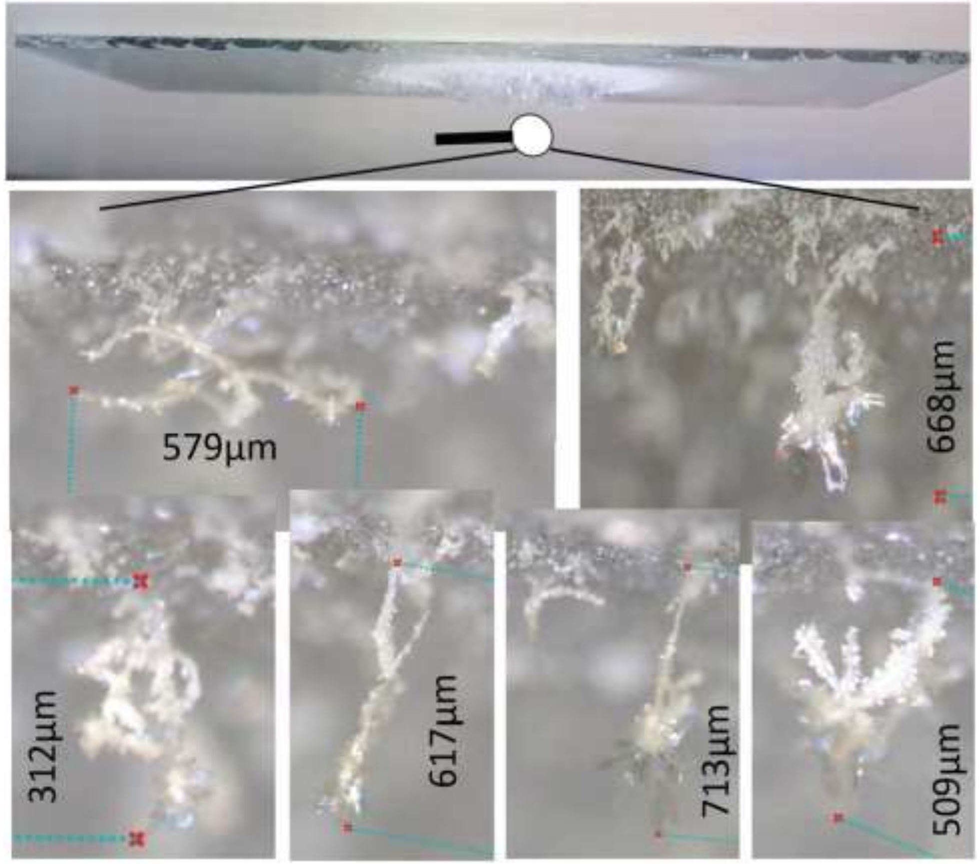
- **Experimental Setup**
  - Bottom glass plate
  - Two spacer 2mm
  - Top glass plate
  - Metal powder on bottom glass plate
  - Temperature top plate approx. 20°C below bottom plate
- **Temperatur profile similar to TGA measurement**
  - Variation of T-max and hold times



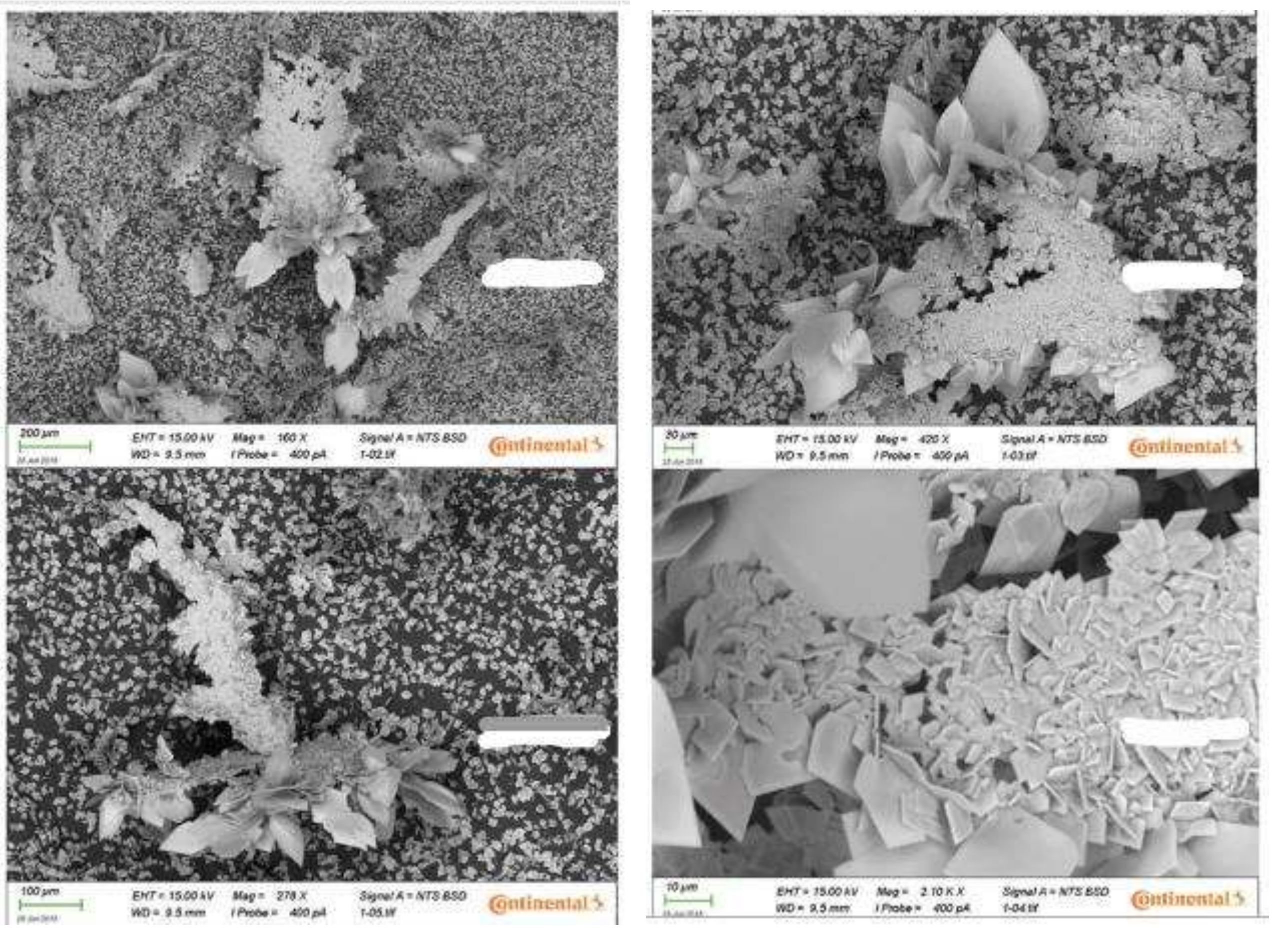
Metall Formiate Evaporation

Christall formation on top plate using SAC

- **Chrystal's grow on the top surface (SAC)**



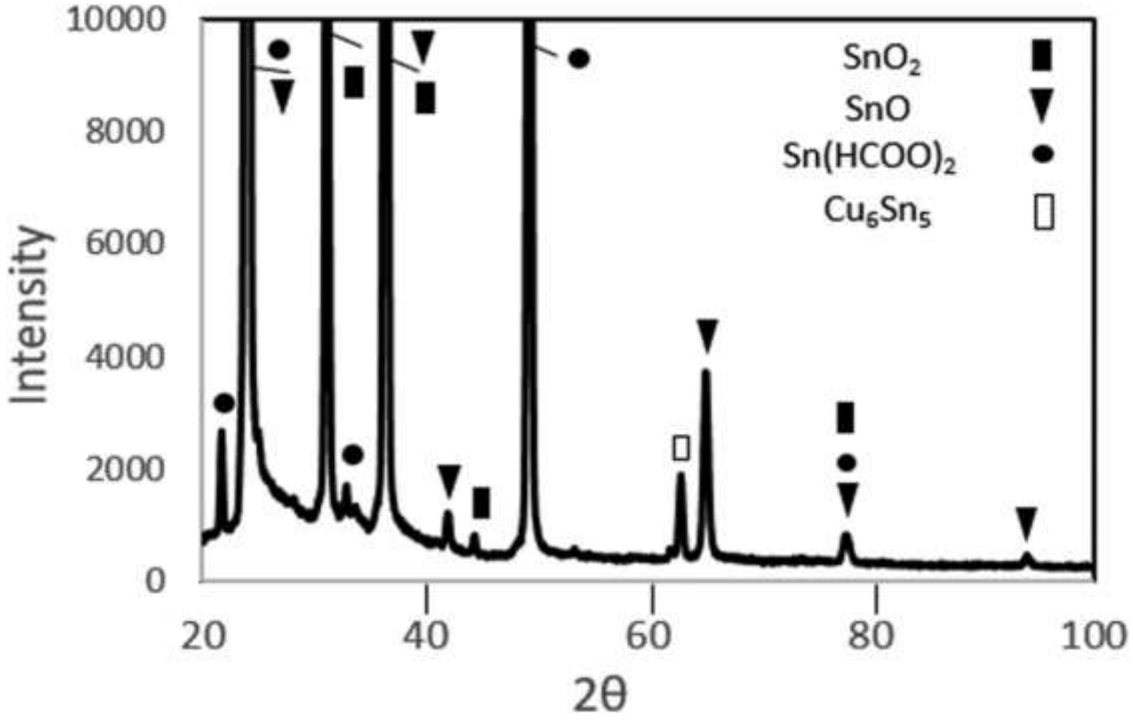
3D optical microscope



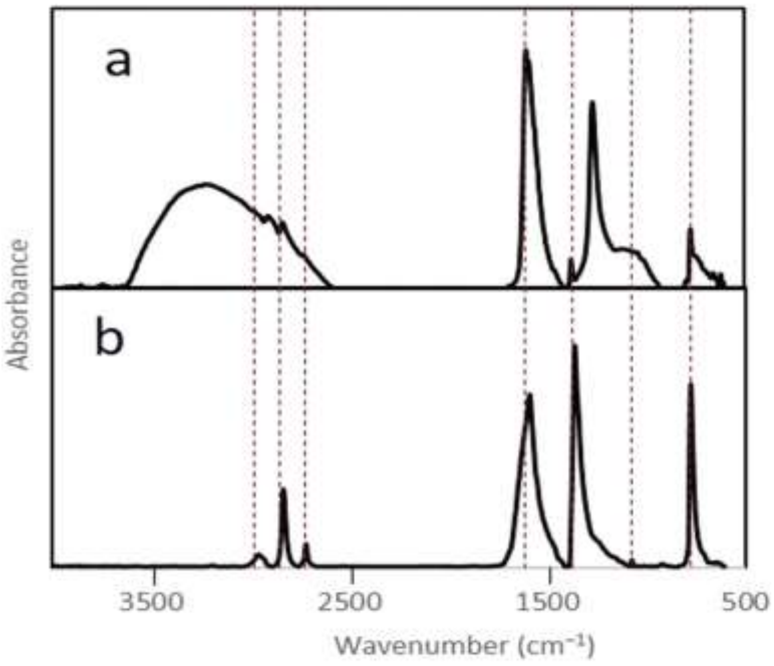
SEM microscope

Metall Formiate Evaporation

Analysis of crystals



XRD analysis



FT-ATR Infrared spectroscopy

a) Measured b) reference NaHCOO

Metal Formiate Desorption

Transportation process by formiate desorption

- **Adsorption around 150^{o}C - 190^{o}C**

$$SnO_2 + i\,HCOOH \leftrightarrow Sn(COOH)_i + H_2 + O_2$$

$$SnO(s) + i\,HCOOH(g) \leftrightarrow Sn(COOH)_i(s) + H_2O(g)$$

$$Sn(s) + i\,HCOOH(g) \leftrightarrow Sn(COOH)_i + H_2$$

- **Desorption around 200^{o}C - 215^{o}C**

$$Sn(HCOO)_i\,(s) \leftrightarrow Sn(HCOO)_i\,(g)$$

- **Decomposition around 200^{o}C - 215^{o}C**

$$Sn(HCOO)_i \leftrightarrow Sn + CO_2 + H_2$$

$$Sn(HCOO)_i \leftrightarrow SnO + CO_2 + H_2CO$$

- **Carbonate formation**

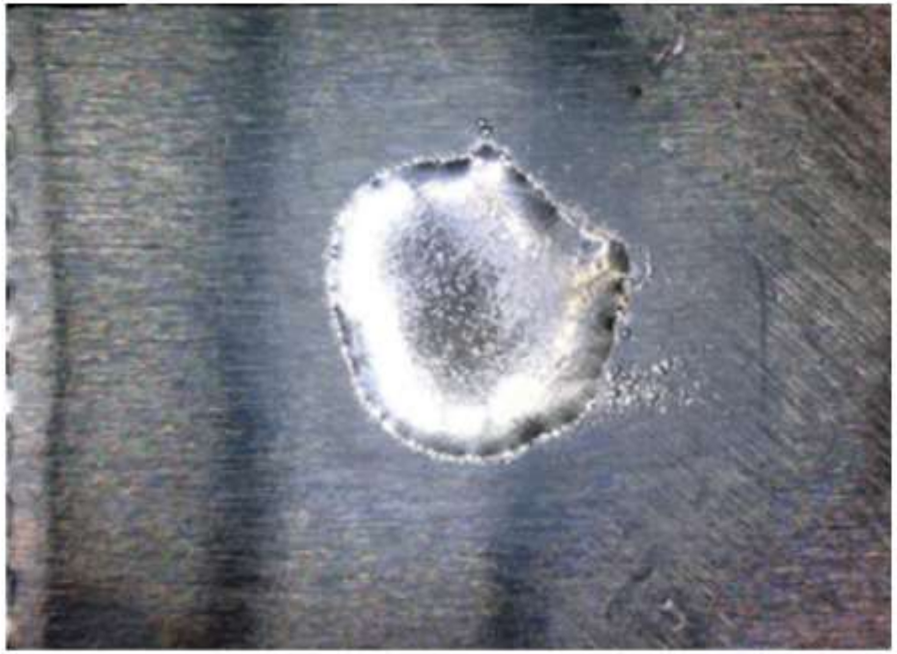
$$Sn(COOH)_2 \leftrightarrow SnCO_3 + H_2CO$$

$$SnCO_3 \leftrightarrow SnO + CO_2$$

Contamination

- **Metall deposition can be observed around SAC powder on copper for formic acid driven solder process**

Solder Paste with standar resin containing flux

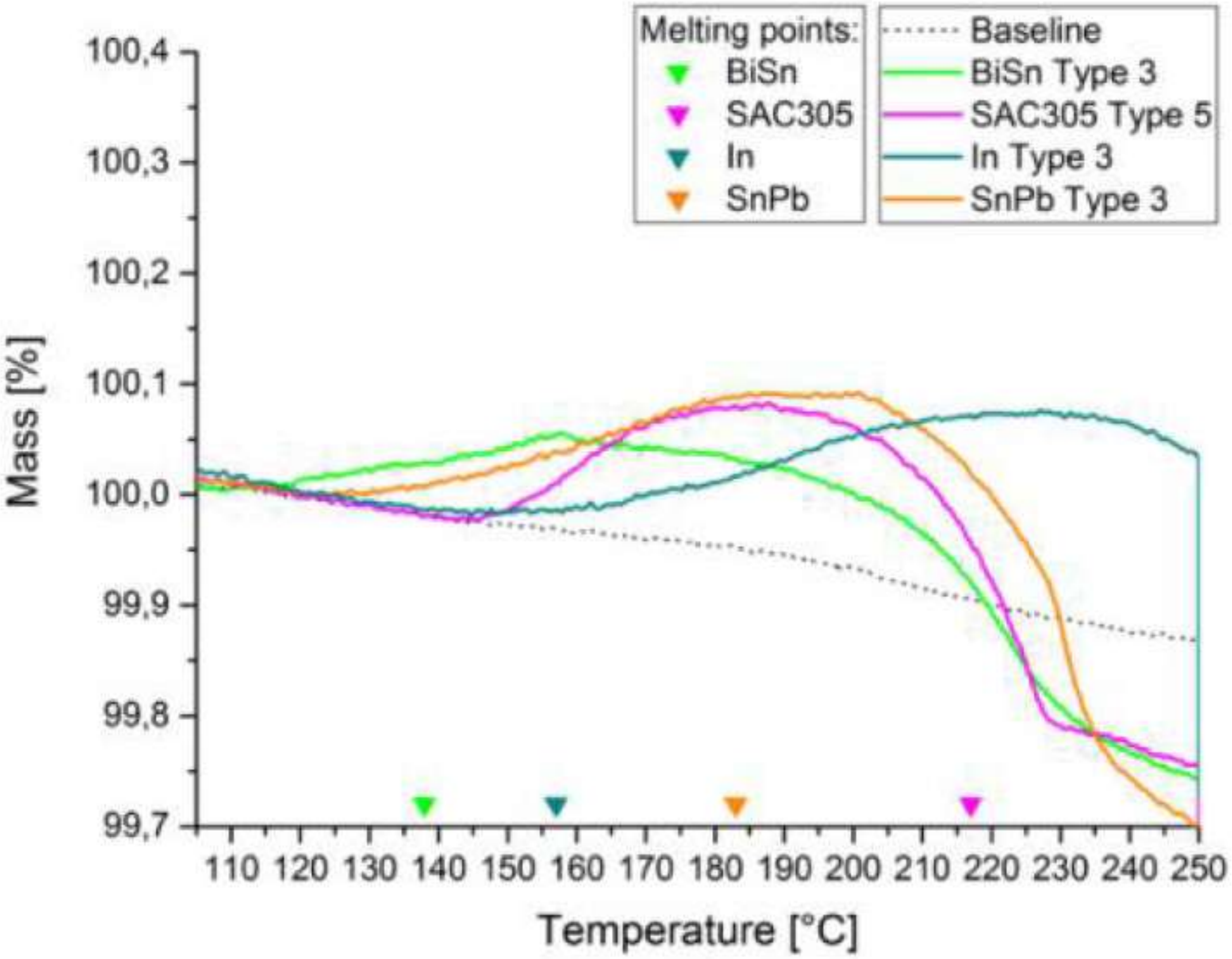


Pure organic carrier

Formiate Formation and Desorption

SAC305 – BiSn – In - SnPb

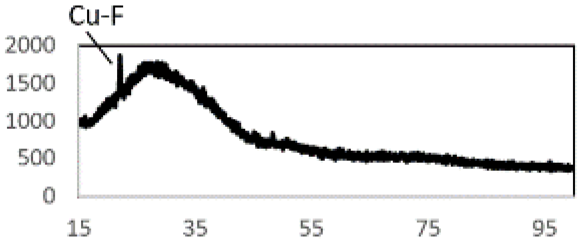
- **Formiate formation and desoption / decomposition depends on metal**



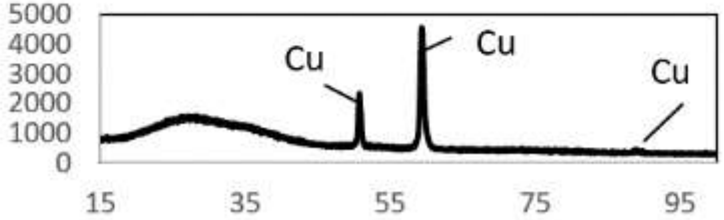
Metal Formiate Evaporation

Christal formation on top plate using Copper

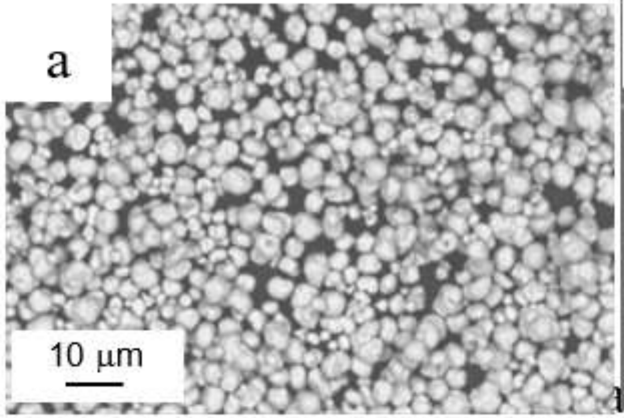
- **Chrystal's grow on the top surface (Copper)**



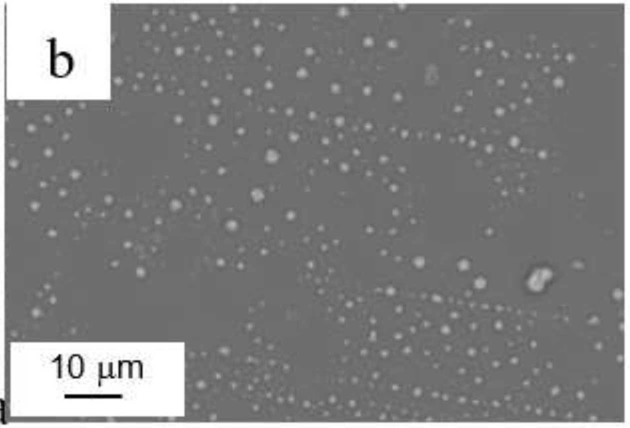
XRD: taken out before heating to 240°C



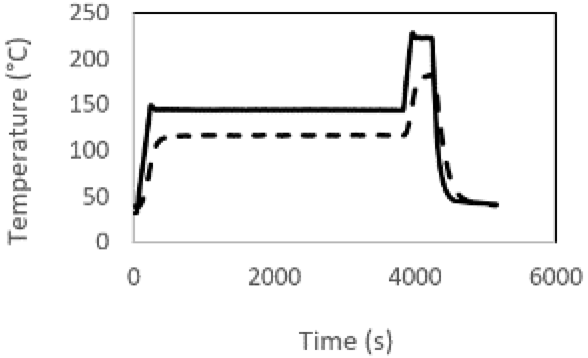
XRD: after 240°C

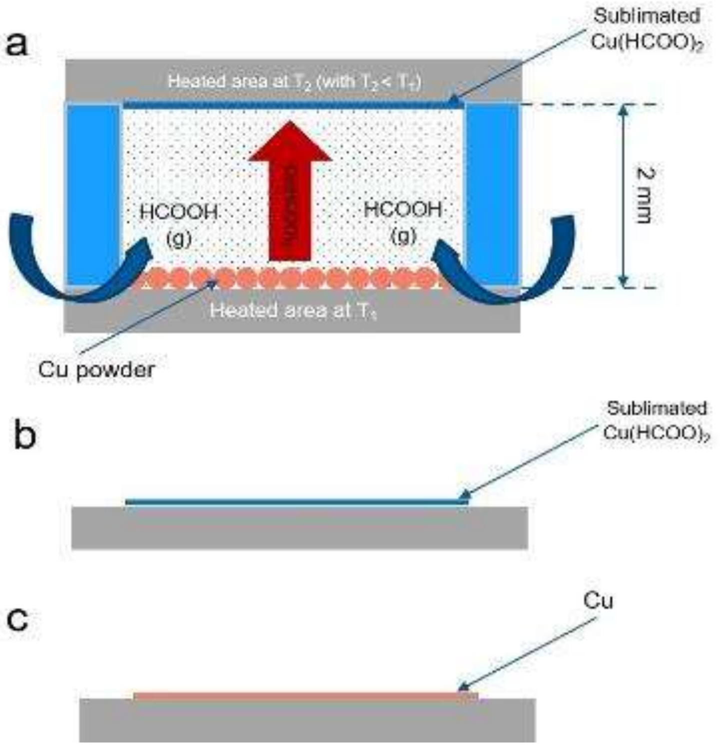


Copper powder bottom



Copper deposition top





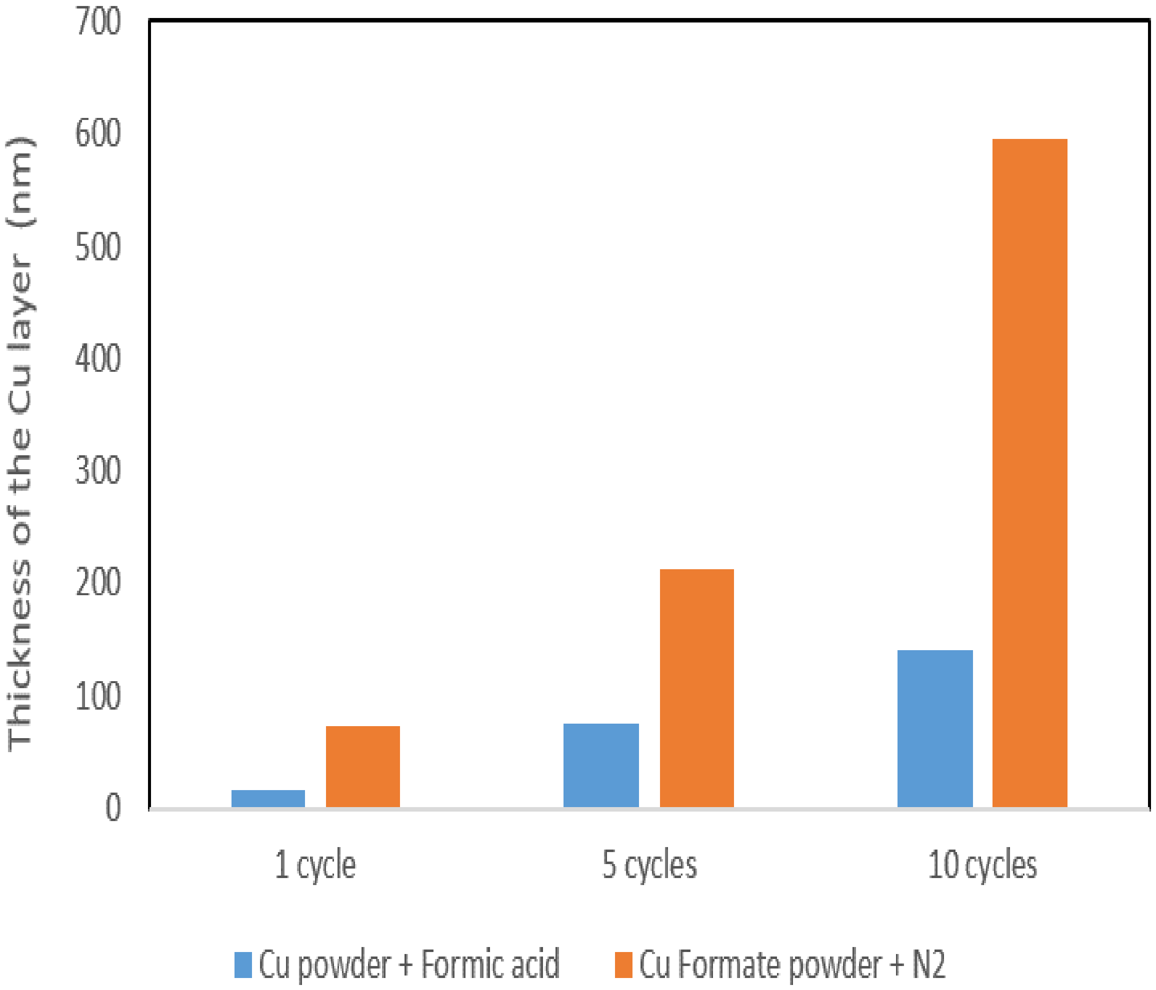
Chemical Vapor Deposition (CVD) of Copper

CVD Based on gaseous copper formiate chemical vapor deposition of copper

- **The CVD process for copper based on desorbed formiate is known**

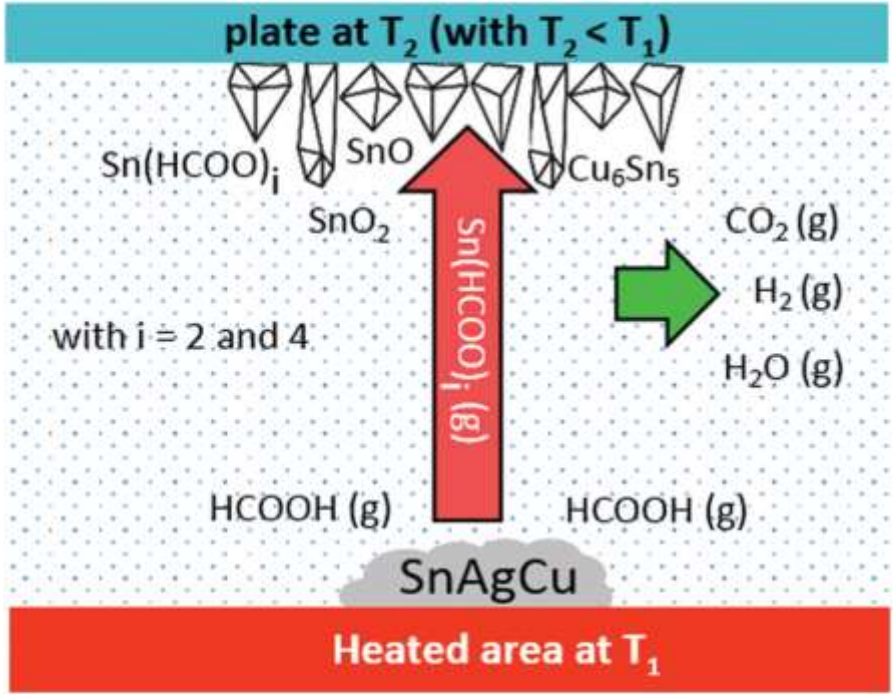
  M. S. Polyakov, A. M. Badalyan, V. K. Vasiliy and I. K. Igumenov, Thermal- and Plasma-Enhanced Copper Film Deposition via a Combined Synthesis-Transport CVD Technique, Chem. Vap. Deposition 2014, 20, 170–176.

  - Argon gas is At 120°C – 140°C / 10mbar argon gas enriched with formic acid is conducted via copper
  - Gas is afterwards conducted over a 220°C-300°C hot surface
  - Copper is deposited on the surface
- **Experiment in reflow oven at athmospheric pressure:**
  - Nitrogen enriched with formic acid
  - Evaporation at 150°C
  - Decomposition at 240°C
  - Copper powder and copper formiate powder



Conclusion

- **Desorption of metal formiate is observed**
- **Metal formite decomposes also in the same temperature range**
- **Risk of metal, metal oxide and carbonate contamination due to decomposion of gaseous metal formiate**
- **To enable clean process**
  - Binder of flux reduces outgasing of metal formiate
  - Process parameter adjustment (pressure, temperature formic acid concentration)



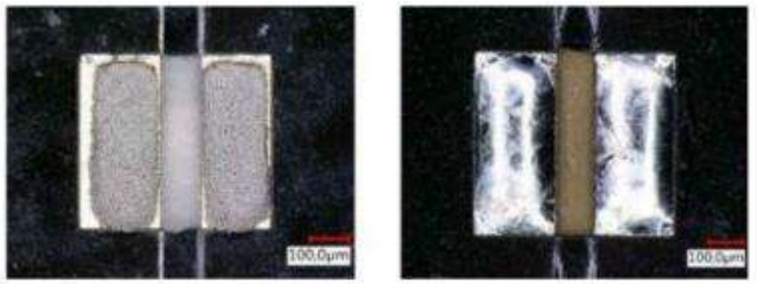
Introduction

AuSn Solder Process under Formic Acid

Fluxfree Soldering with SAC paste

- **SAC305 Type 5 solder powder in flux-free carrier medium**
- **Solder paste priniting**
- **Reflow under formic acid**

Figure 12 Pictures of a fluxless SAC305 solder paste after reflow without reducing atmosphere (left picture) and with gaseous activator (right picture) (magnification: 60x)



Residual free solder process for fluxless solder pastes, 217, Soldering & Surface Mount Technolog, https://doi.org/10.1108/SSMT-10-2017-0030

Figure 2 The principle of fluxless soldering with a preform (left picture) and fluxless solder paste (right picture)

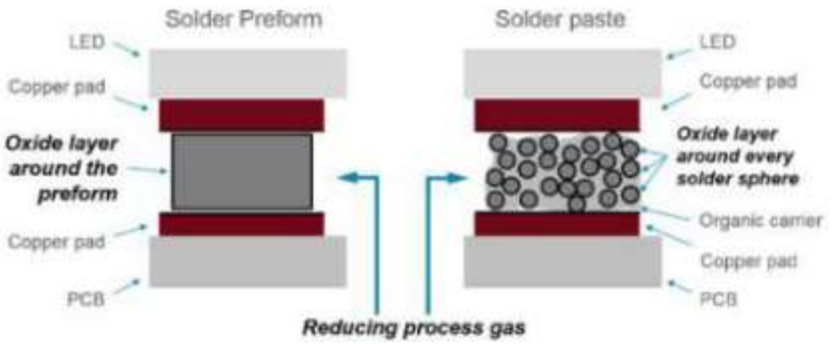
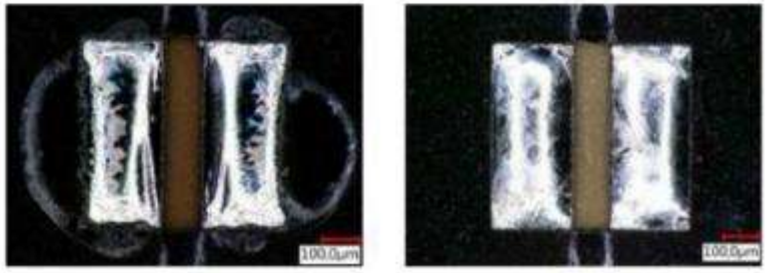


Figure 6 Optical inspection of the solder joint soldered with conventional flux solder paste (left picture) and a sample soldered with fluxless solder paste (right picture) (magnification: 60x)



Thermo Gravimetric Analysis

- **Investigation of different solder and copper powder under formic acid enriched nitrogen**

$$MeO(s) + HCOOH(g) \rightarrow Me(COOH)(s) + H_2O(g)$$

$$Me(COOH)(s) \rightarrow Me(s) + CO_2(g) + H_2(g)$$

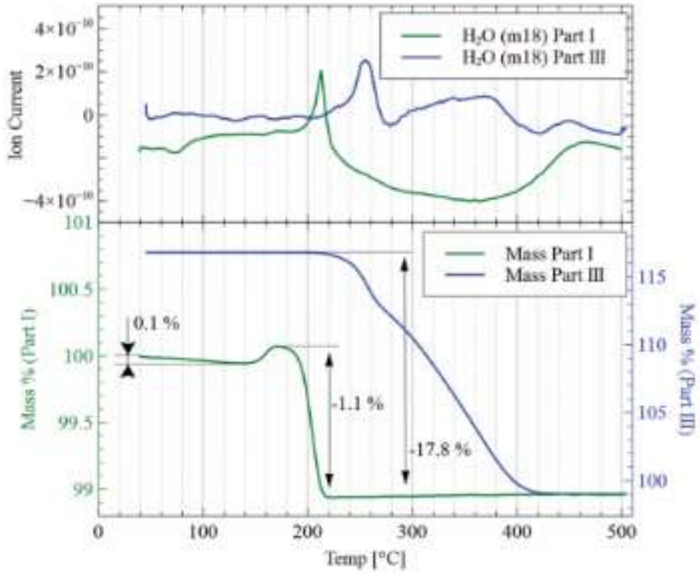
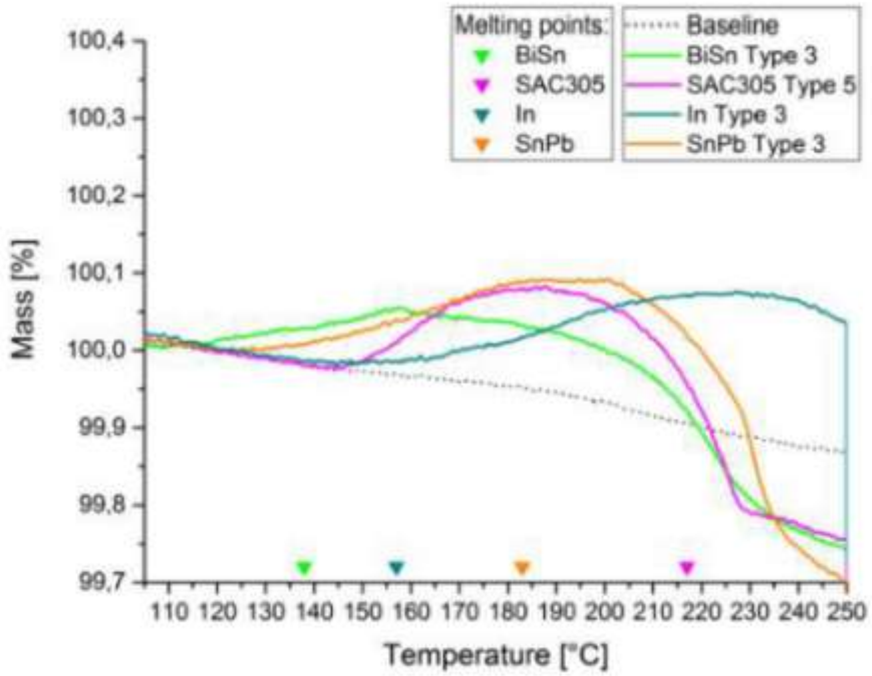


Fig. 5 Comparison of the results obtained using formic acid on the pristine copper powder (green lines, process in region I) and on the fully oxidised copper powder (blue lines, process in region III). Top: Mass signals of water. Bottom: TGA profiles (the signal of mass part I is magnified by a factor 9).

Fosca Conti, Alexander Hanss, Carolin Fischer, Gordon Elger, Thermogravimetric investigation on the interaction of formic acid with solder joint Materials, New Journal of Chemistry, 201640, 10482--10487

Figure 10 Results of the TGA and the melting points of different solder alloys



Thanks for your attention

- Contact: Gordon.elger@thi.de