ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Structuration of thin bridge and cantilever structures in thick-film technology using mineral sacrificial materials

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Outline

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1. Introduction - Thick-film / LTCC structuration techniques
2. Mineral sacrificial pastes - Requirements & formulation
3. Overlying structures - Overprinting onto porous layers
4. Final steps - Etching, rinsing & drying
5. Conclusions & outlook

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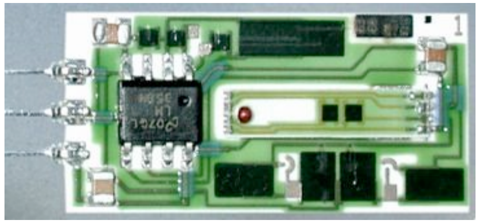
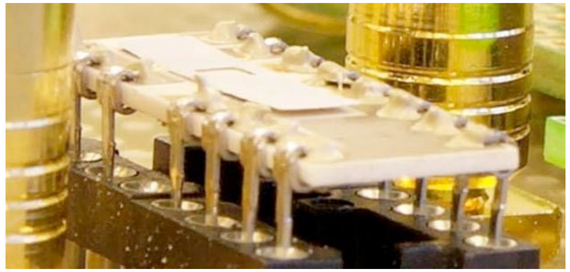
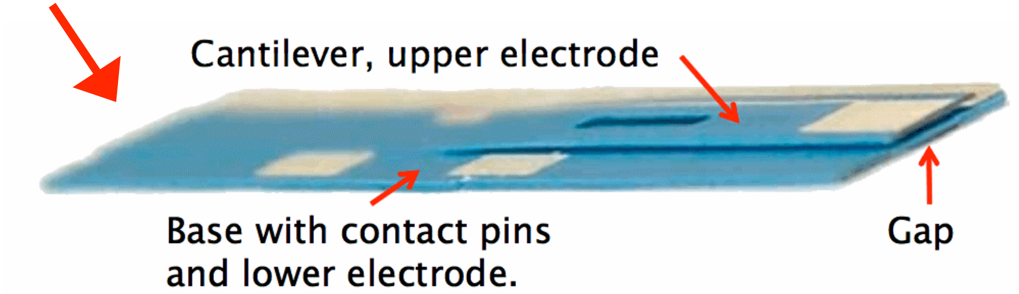
1. Applications : cantilever & bridge

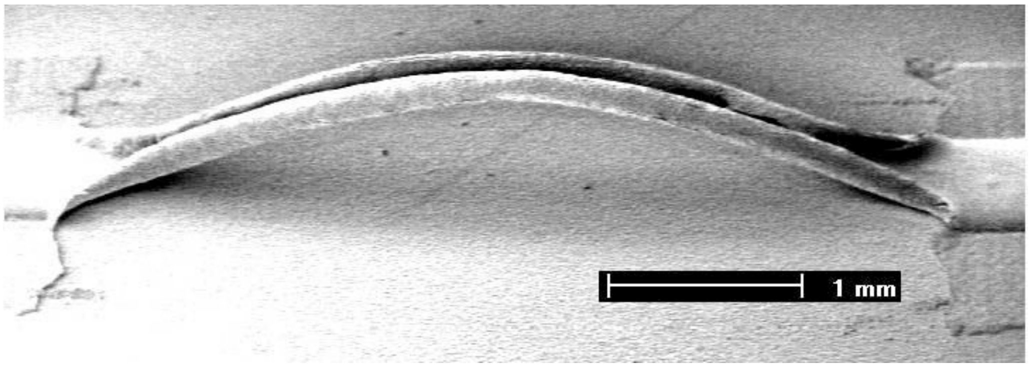
- Micro-force sensors
  - Thick-film or LTCC
  - Mineral sacrificial paste etched by acid





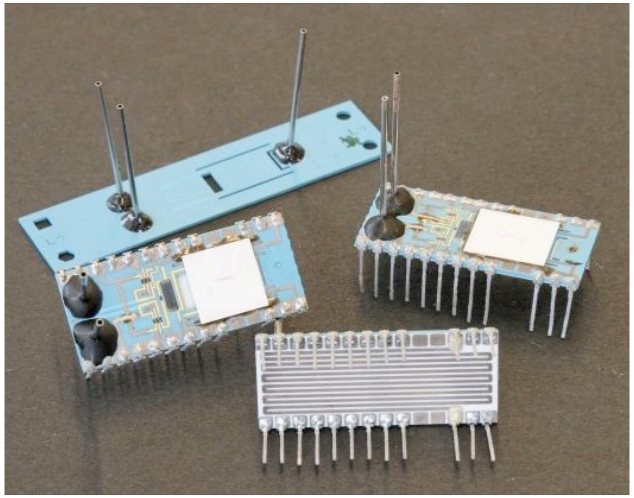


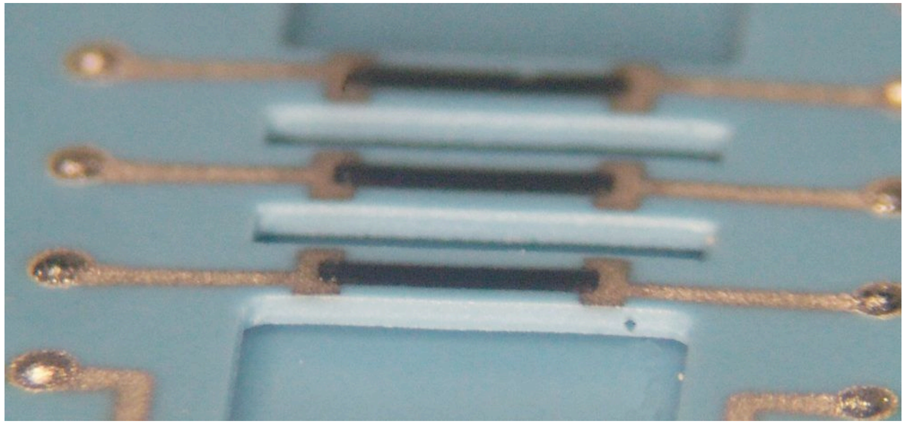
- Suspended thermistor
  - Flow sensing
  - Thermal actuator
  - Igniter
    - μ-Thruster
    - SOFC

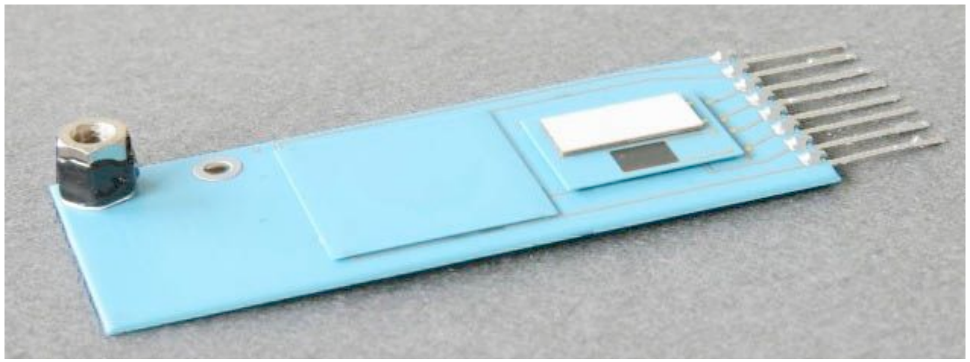


1. Applications : fluidics

- Chemical reactor
- Flowmeter
- Gas viscosity sensor







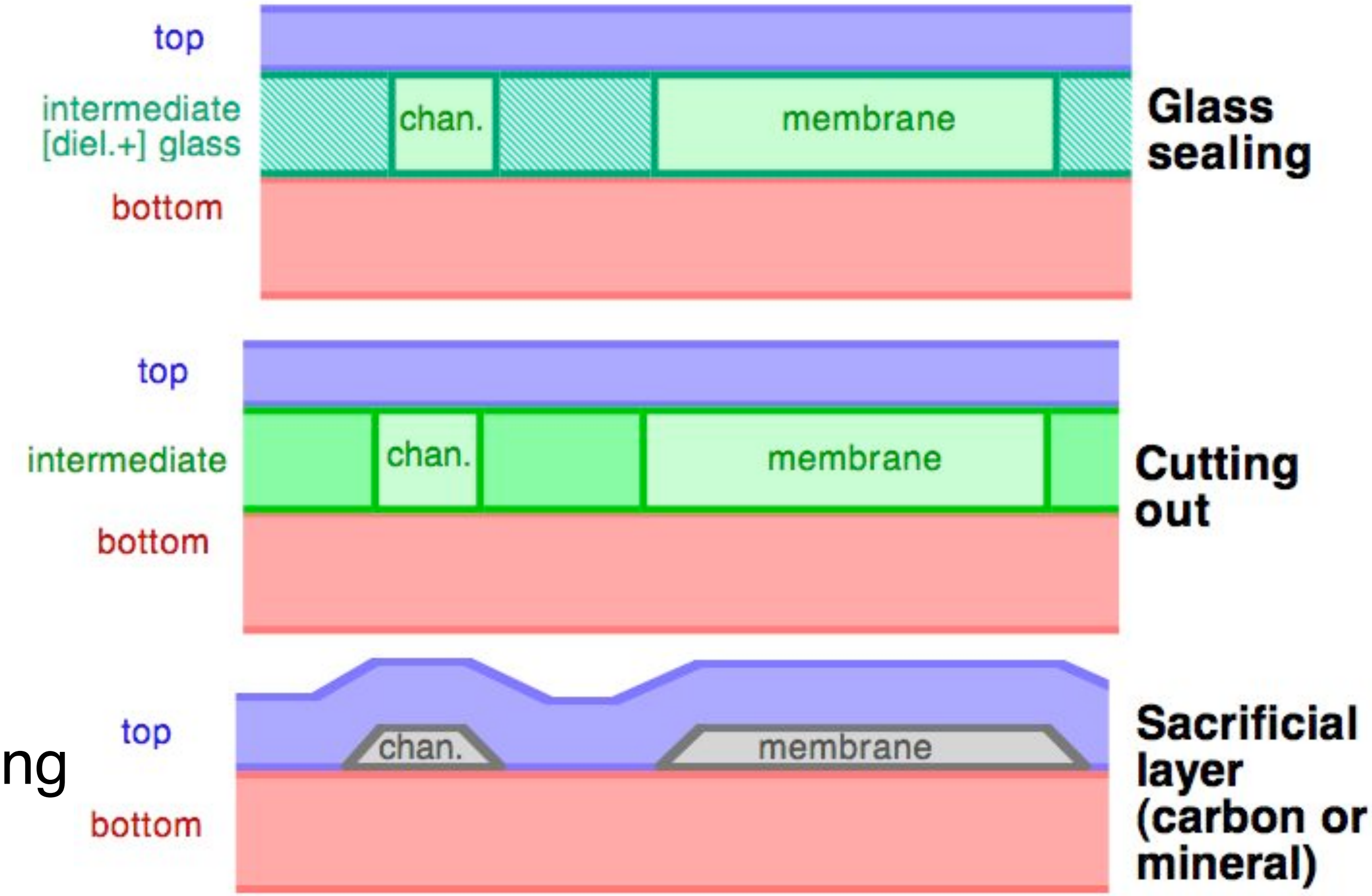
1. Structuration methods

Features

- Vias
- Channels
- Membranes
- Beams

Three types

1) Glass sealing
2) Cutting & stacking
3) Sacrificial layer



1. LTCC vs. alumina for sensors

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Material	LTCC (DP 951)	Al_2O_3 (96%)	Ratio
Minimal thickness [mm]	0.04	0.17	*0.24*
Short-term strength [MPa]	320	600	*0.53*
10 year strength [MPa]	110	270	*0.41*
Young's modulus [GPa]	110	320	*0.34*
Thermal conductivity [W/m]	3	25	*0.12*
Design strain [ppm]	1'000	800	*1.25*
Flexural sensitivity [kN^{-1}]	5.68	0.11	*53*
Thermal resistance [K/W]	8'333	235	*35*

- LTCC for thermal & low-range mechanical sensors
- Thick-film dielectric ≈ LTCC

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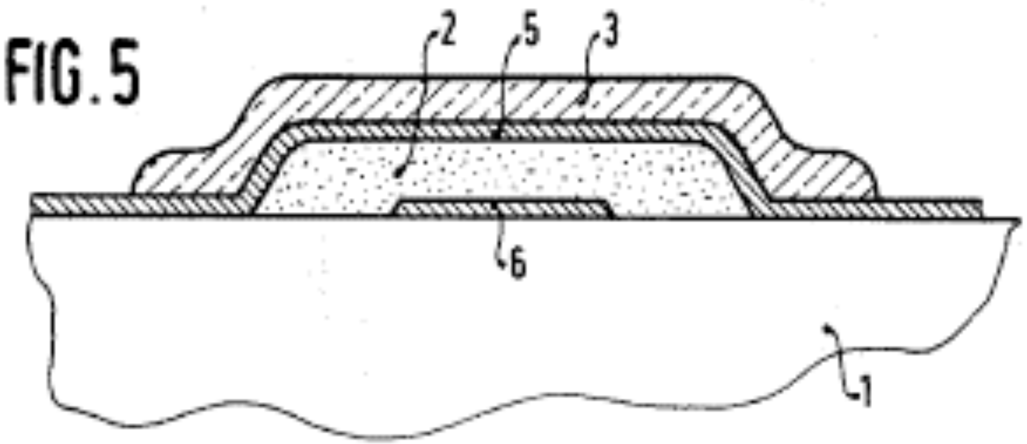
2. Mineral sacrificial paste vs. carbon

- Pioneering work in in the 1980's
  - Stecher et al., Bosch, Germany
  - Thick-film dielectric on carbon sacrificial paste
  - Alumina substrate
  - Complex steps to avoid sagging / swelling (N_2, then air)
  - Already thought about using mineral sacrificial paste (MSP)!

➢ Did not catch on

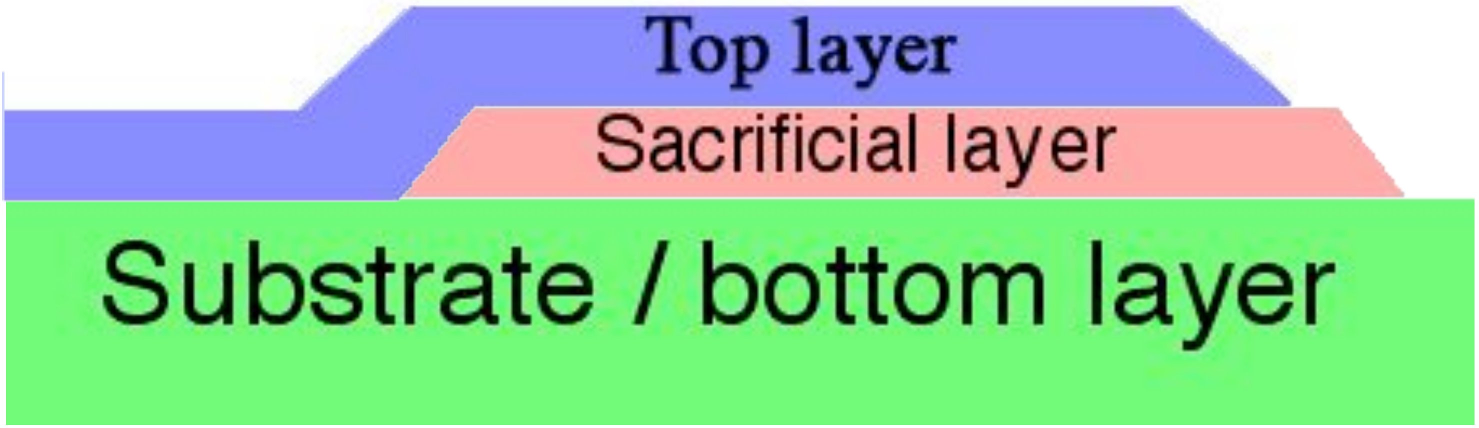
FIG.5



2. Mineral sacrificial paste - process

- Print [fire] mineral sacrificial paste (MSP) onto LTCC / ceramic substrate
- Laminate (LTCC) / print (ceramic) top layer
- Fire structure (co- or post-fire)
- Chemically etch sacrificial layer

→ Requires relatively "open" structure

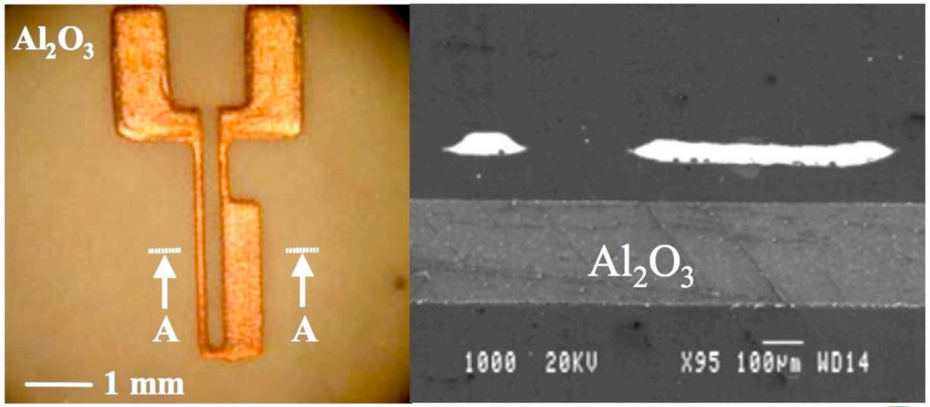


2. Previous MSP work

- 1983 : Stecher & al. - **Cu** : OK only with N_2
- 2004 : Sippola & al. - **Au**? (not mentioned, metal etched with KI)
- 2006 : Birol et &.; 2006-7 Lucat & al - $CaCO_3$ & $SrCO_3$
  - $CaCO_3$ dissociates to CaO + CO_2, then swells to $Ca(OH)_2$
  - $SrCO_3$ doesn't dissociate, but CO_2 evolved in acid etching
  - No cohesion / sintering: not all-purpose

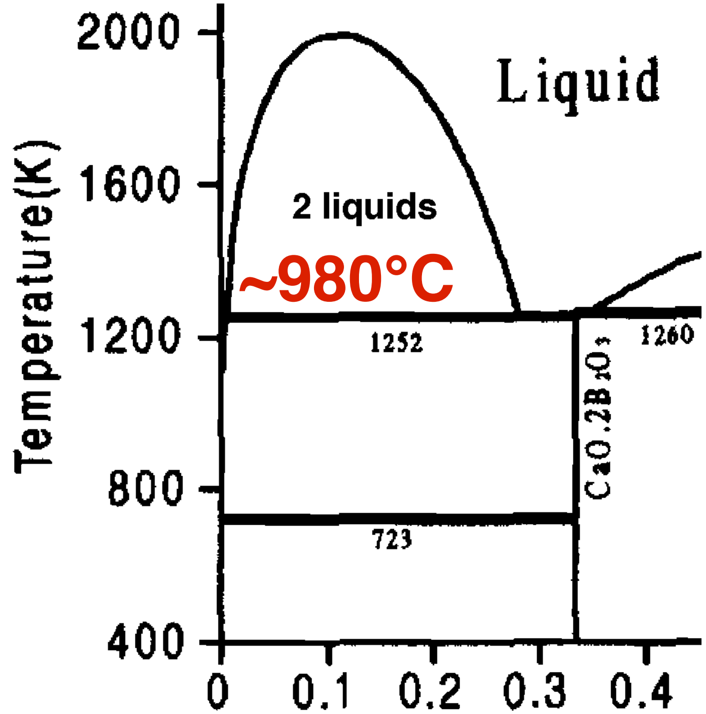
2006 Birol (LTCC)

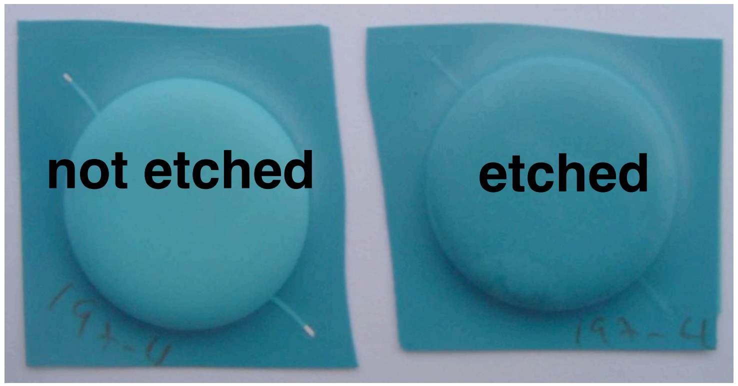
2007 Lucat (Thick-film)



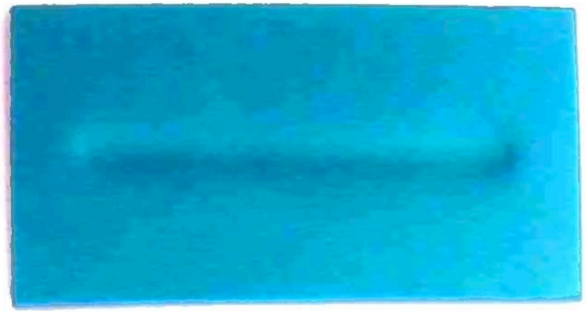
2. MSP - $CaO + B_2O_3$

- CaO or $CaCO_3$ + B_2O_3 or borax ($Na_2B_4O_7$)
- **CaO - B_2O_3** : low shrinkage (ca. 8%)
- Sintering hindered by CaO-B_2O_3 reaction?
- Deformed LTCC (low shrinkage)
- Very good dissolution in acids
- Low cohesion & swelling in humid air





Sintered LTCC + paste



2. MSP - CaO + borax

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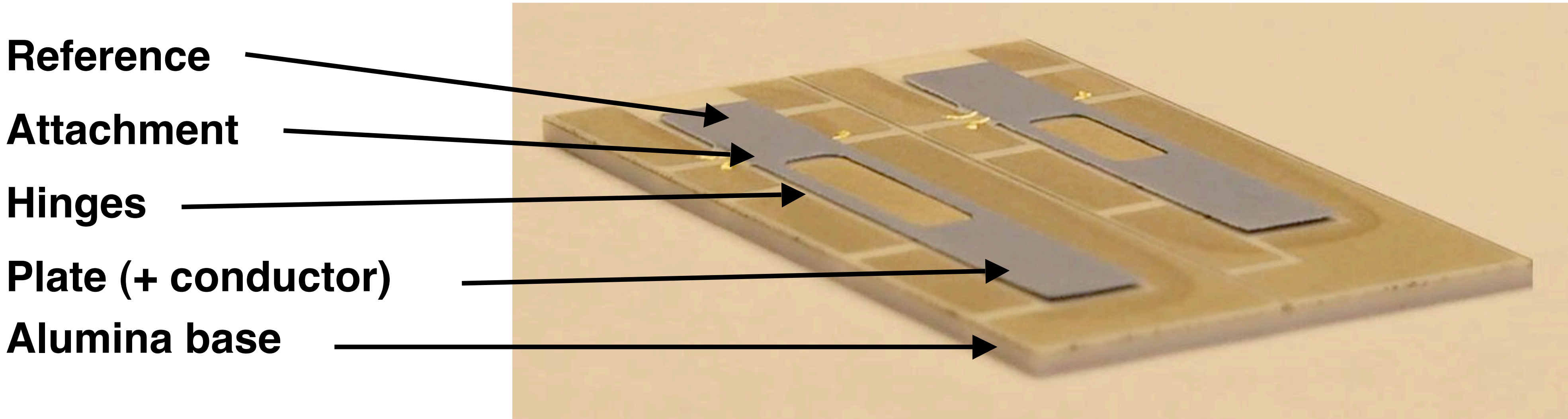
- B_2O_3 replaced by borax ($Na_2B_4O_7$)
  - Reduced B_2O_3 volatility
  - Melting at ~740°C
- Dense & good cohesion @ high borax : **overprinting possible**

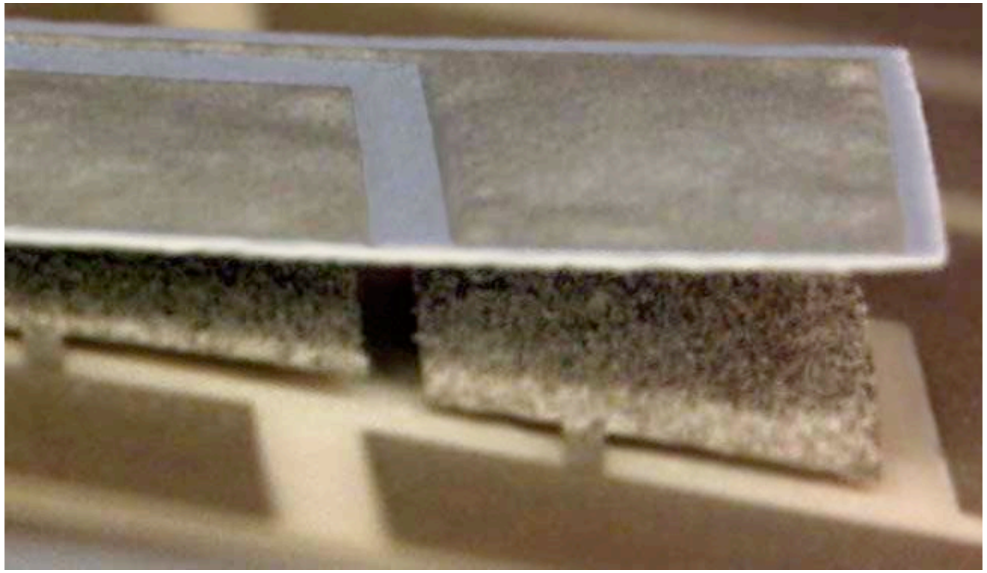
→ **Capacitive force sensor** (thick-film dielectric + conductor)

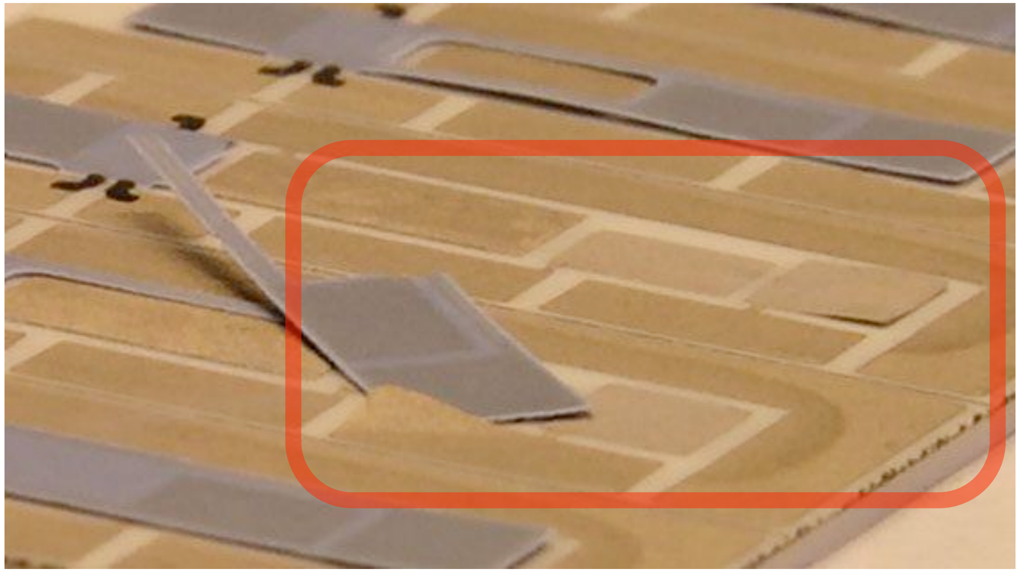


2. MSP - issues with borax

- Strong reaction with LTCC & thick films (Na)
- Difficult to remove by etching
- Peeling of conductor under sacrificial paste upon etching (Na)

→ **Only small amounts of alkali oxides allowable**





2. Paste formulation vs. process

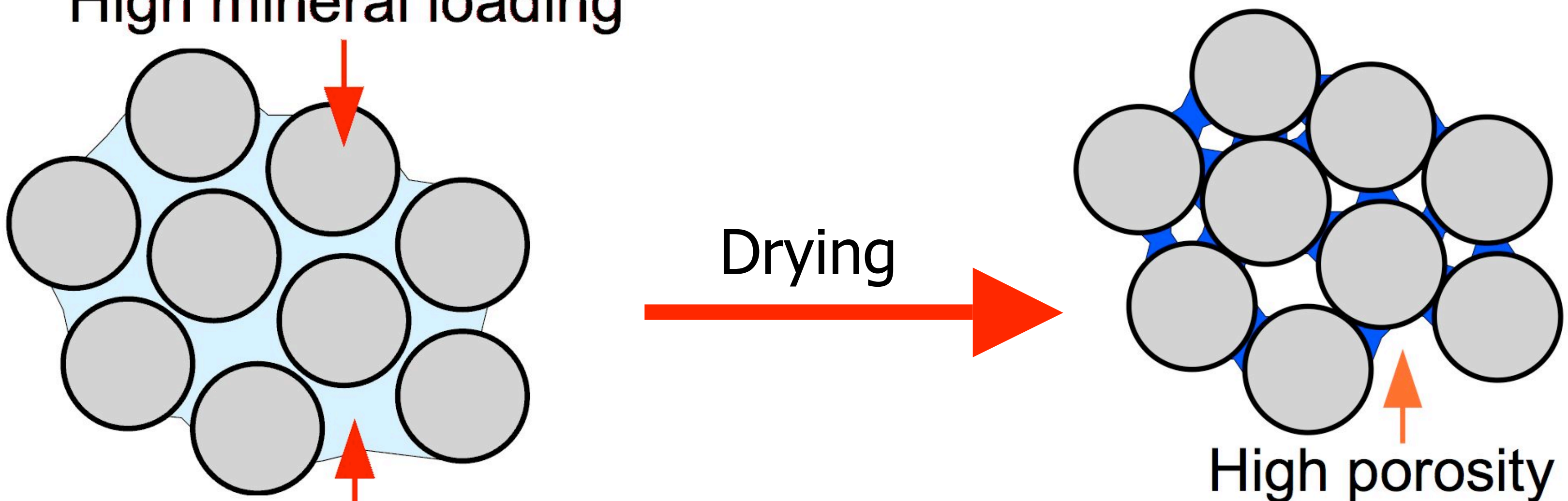
- **Co-firing of MSP with top dielectric / LTCC**
  - LTCC: MSP solvent should not be too aggressive with tape
  - Thick-film: non-porous as-dried MSP **or** pore-tolerant top layer
    - Non-porous MSP: high-binder + other "non-evaporable" organics
    - Pore-tolerant top layer: more viscous vehicle + lower mineral filling

- **Post-firing of dielectric onto MSP**
  - Most straightforward process, better shape control
  - Non-porous MSP too hard to etch
  - Requires pore-tolerant overlayer

2. Low-porosity (as-dried) MSP

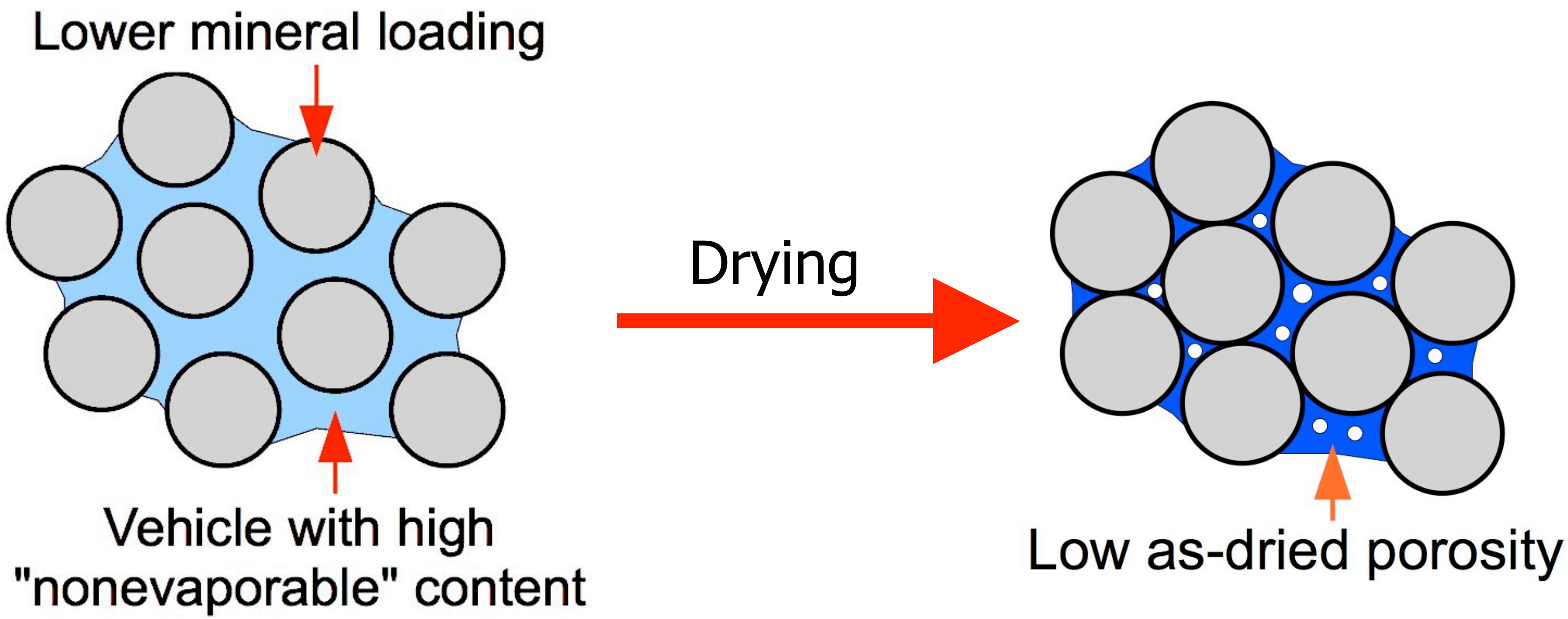
- **Avoid drying of overlayer during printing**
- Non-solvent resin (2007 Lucat: epoxy)
  - Works well
  - Limited shelf life
- Solvent system: aim for denser dried film:
  - Lower mineral filling: works, but not desired solution
  - Increase "non-evaporable" organic part in vehicles
  - "Non-evaporable" organics
    - Polymer binder: low-viscosity grades @ higher concentration
    - Low-molecular weight high-boiling liquids or solids

2. Standard paste formulation



- Low amount of vehicle with little binder
- High as-dried porosity
- Will prematurely dry overlayer with standard formulation

2. Formulation for dense as-dried layer



- Higher amount of vehicle (lower powder loading)
- Increase nonevaporables: low-MW polymer + organics
- Low as-dried porosity: overprinting with standard paste

2. Sacrificial mineral: MgO

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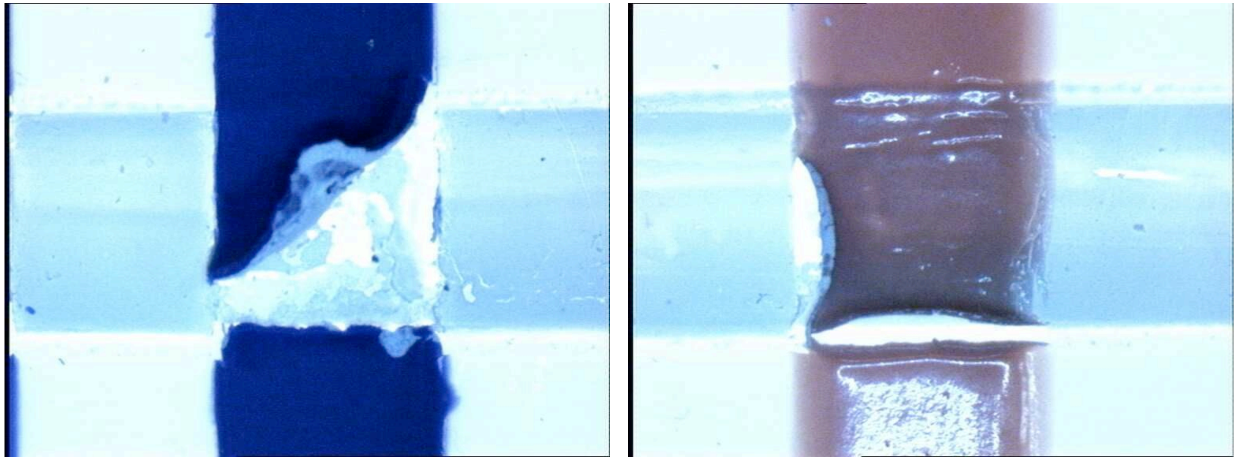
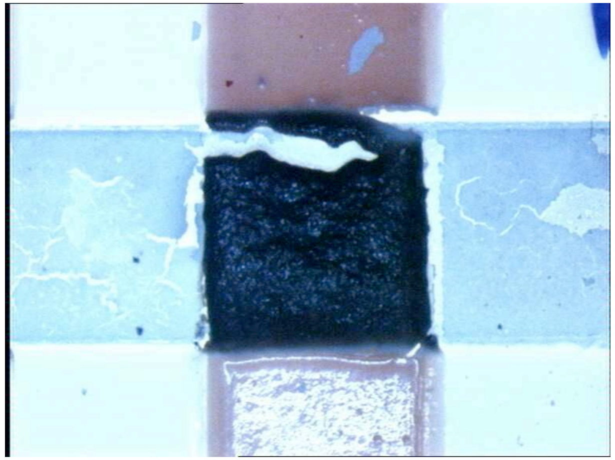
- **MgO - magnesium oxide**
  - Alkaline earth oxide - similar to CaO / SrO
  - Oxide reasonably stable vs. humidity ("dead burned")
  - Well-known in MEMS literature (surface micromachining)
  - Etchable in H_3PO_4 & acetic acid
  - No carbonates
    - No decomposition during firing
    - No CO_2 gas generation during etching
  - No sintering → **needs sintering aids**
    - $H_3BO_3 \rightarrow B_2O_3$
    - Borax = $Na_2B_4O_7$

2. MgO + H_3BO_3 - co-firing



ESL 4913 (left) / 4903 (right) over MgO+H_3BO_3
Insufficient cohesion of MgO in spite of B_2O_3



ESL 4903 over MgO+H_3BO_3
Too high H_3BO_3: reaction

- H_3BO_3 gives insufficient cohesion in std. formulation
- Evaporation of B_2O_3 → reaction with overlying dielectric

2. MgO + borax - co-firing

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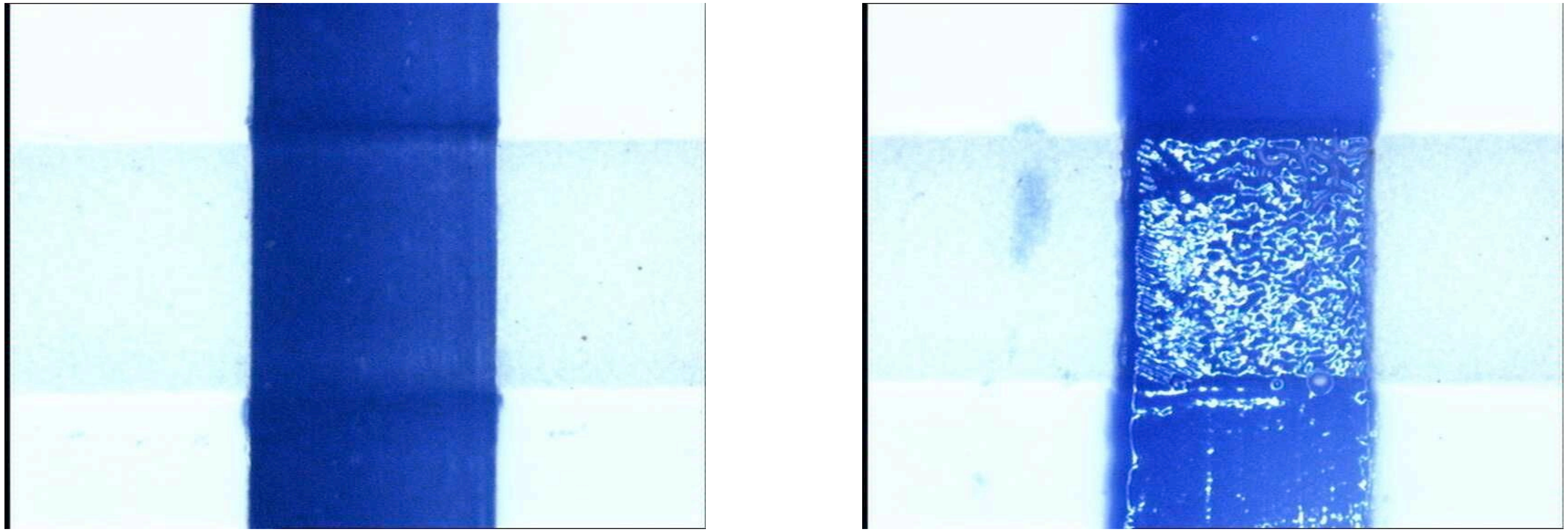
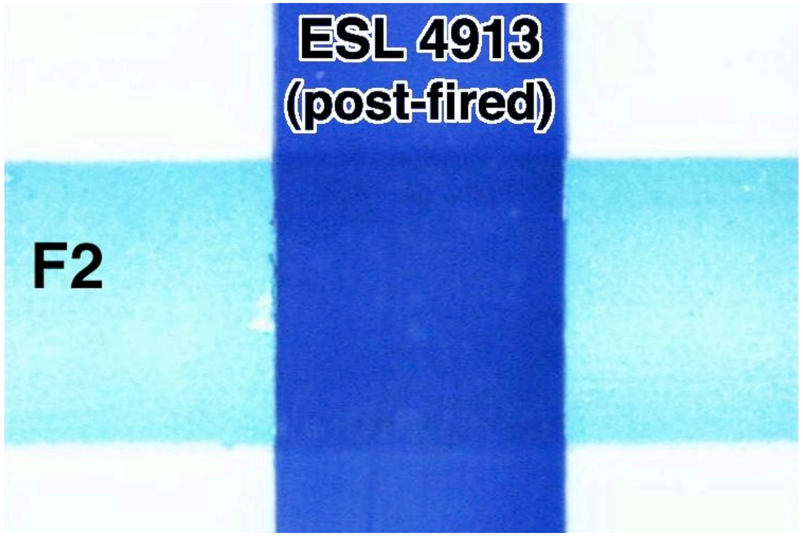
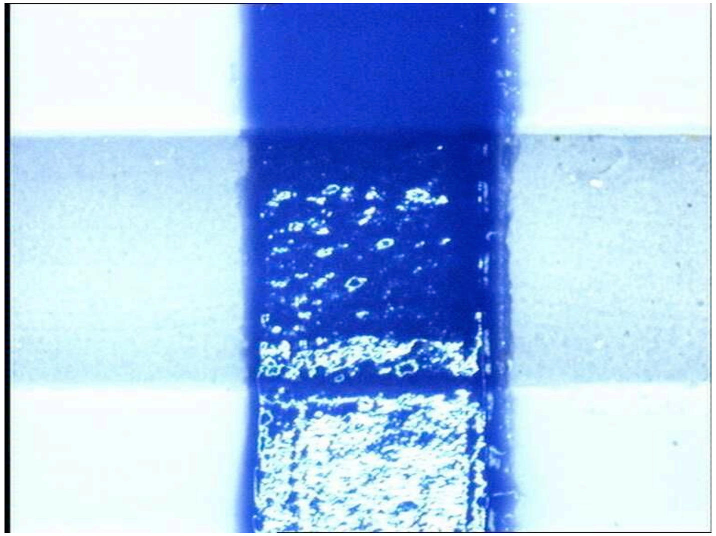


ESL 4913 (left) / 4924 (right) over $MgO+Na_2B_4O_7$
Better cohesion, but some borax enters dielectric

- Borax gives better cohesion in std. formulation
- Some reaction still observed

2. MgO + H_3BO_3 - post-firing

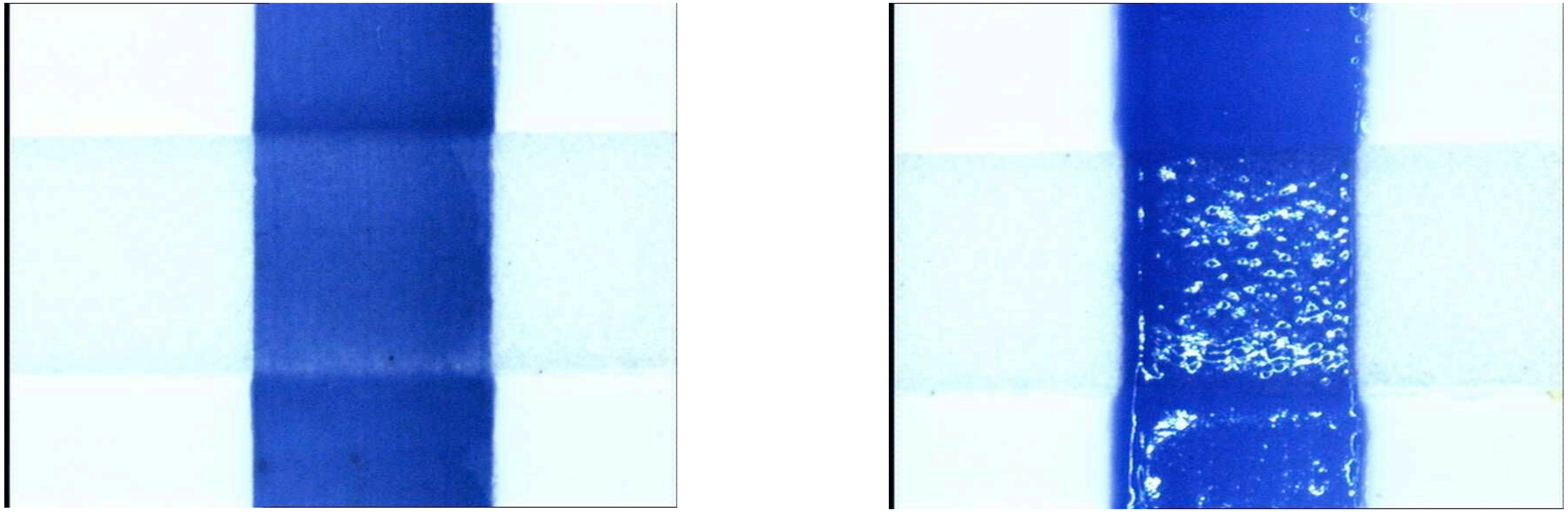




ESL 4913 (left) / 4924 (right) over MgO+H_3BO_3
Sufficient cohesion of MgO with high H_3BO_3 content

- Very high H_3BO_3 gives moderate (sufficient) cohesion
- Excess evaporates → no reaction problems if post-fired

2. MgO + borax - post-firing



ESL 4913 (left) / 4924 (right) over $MgO+Na_2B_4O_7$
OK, still some slight reaction possible

- Post-firing also possible onto borax
- Potential issues (Na+) if MSP printed onto other layer
- Some residual reaction (borax less volatile)

2. Formulation - conclusions

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- **MgO - magnesium oxide**
  - Succeeded in making relatively cohesive sacrificial paste with boric acid / borax (or both) additions
  - Additives only bind the grains - porous layer obtained
  - Reaction problems encountered if co-firing - post OK
  - Low "efficiency" of additives with standard formulation (mixed powders) → **coat MgO particles**
- **Other tests**
  - CaB_2O_4 = calcium borate (or other AE borates)
  - Sacrificial layer or "glue" for MgO

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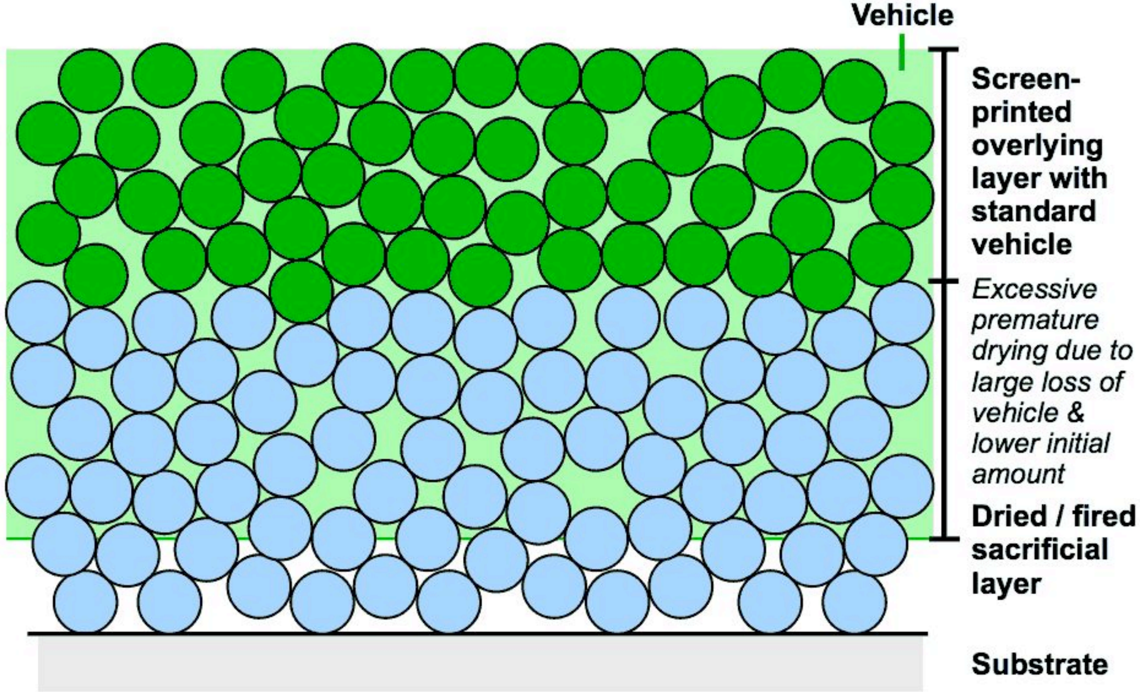
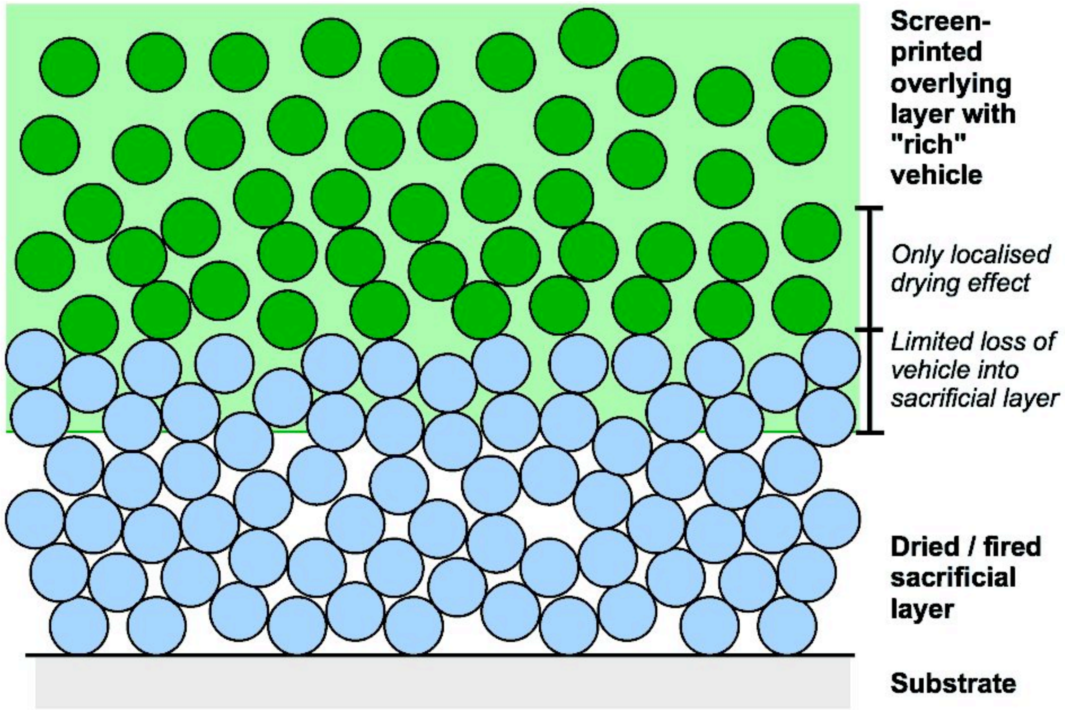
3. Overprinting onto porous layer



- High mineral loading
- Low-viscosity vehicle escapes into MSP pores

- Standard paste: premature drying
  - Insufficient leveling - rough surface
  - Clogging of the screen

3. Overprinting onto porous layer



- Lower mineral loading
- High-viscosity vehicle is slow to go into pores

- Adapted paste formulation
  - Somewhat lower mineral loading
  - Higher vehicle viscosity (doesn't need "non-evaporables")

3. Formulation for printing onto MSP

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- Example formulation
  - Standard Terpineol / dibutyl carbitol (DBC) solvent
  - Standard ethylcellulose (EC; 46 cps, 48% ethoxy) binder
  - Add ca. 40% volume to commercial dielectric paste

Type	Compound	Parts (by mass)
Solvent	Terpineol	10
	DBC	5
Binder	EC-46-48	3

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4. Acid resistance of dielectrics

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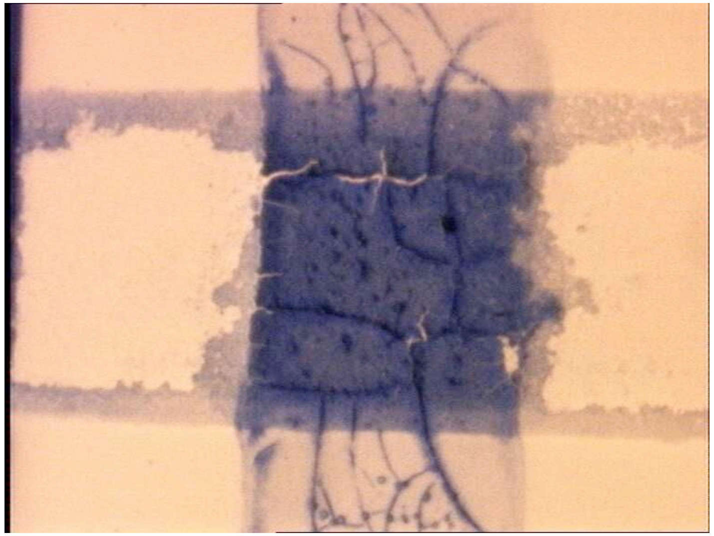
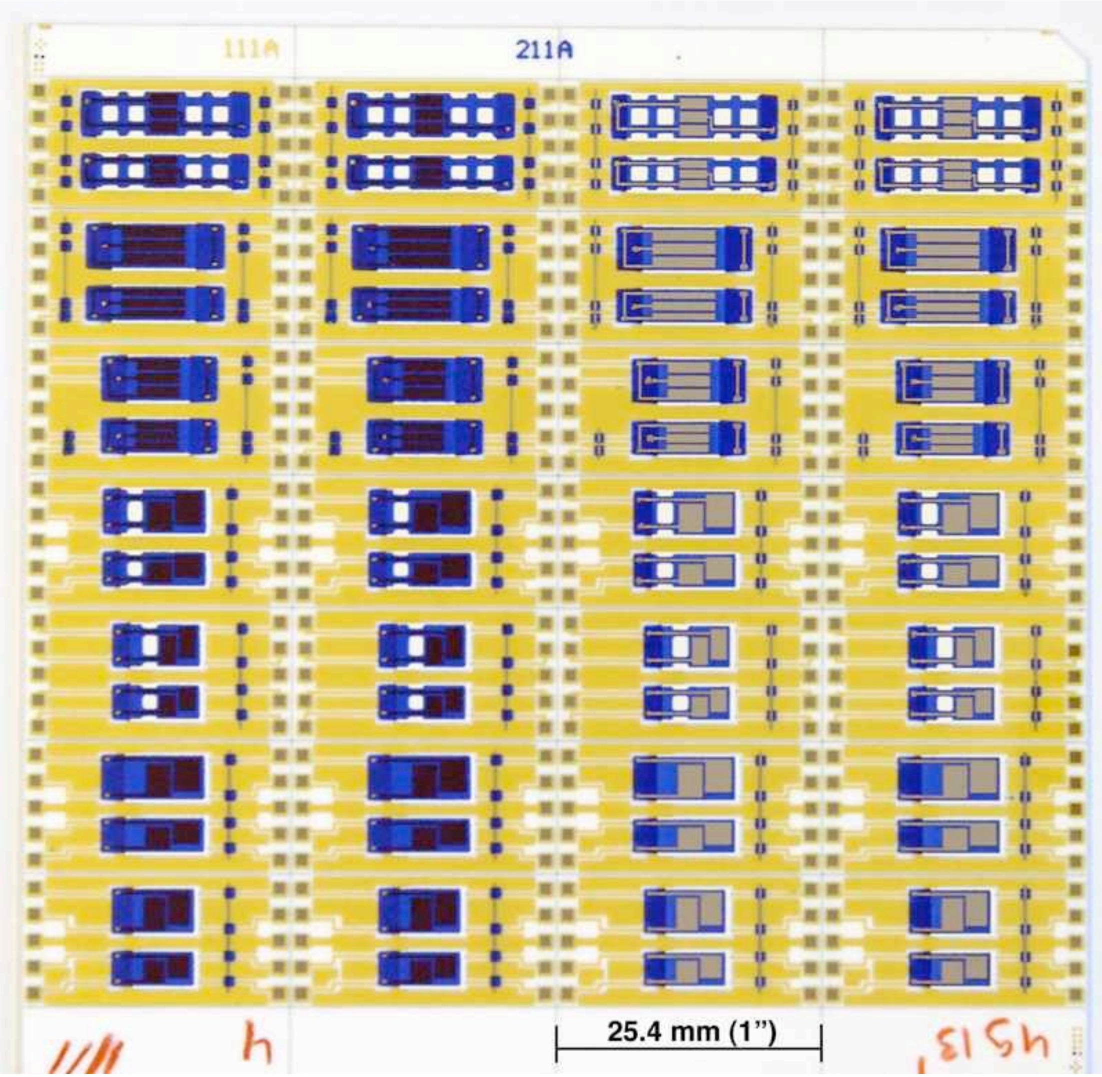


Heraeus GPA 98-029 (left) & ESL 4924 (right) after ≈ 1 day in acid
Failure in 10% acetic or phosphoric acid @ RT

- **Destroyed**: Her GPA 98-029 & ESL 4924
- **Apparently OK**: ESL 4913, ESL 4903, ESL 4904

4. Test structures



- Structures for capacitive force sensors / actuators
- Cantilevers or bridges
- Different width
- Plain or structured (cut-outs)

4. Sacrificial layer removal

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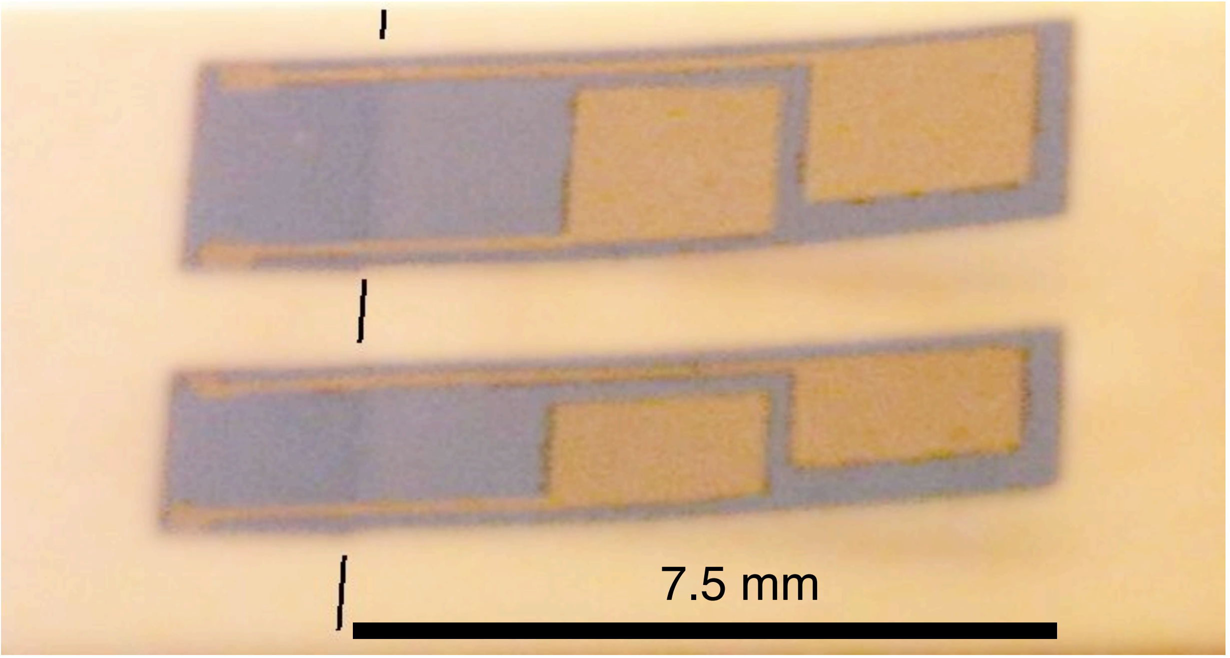
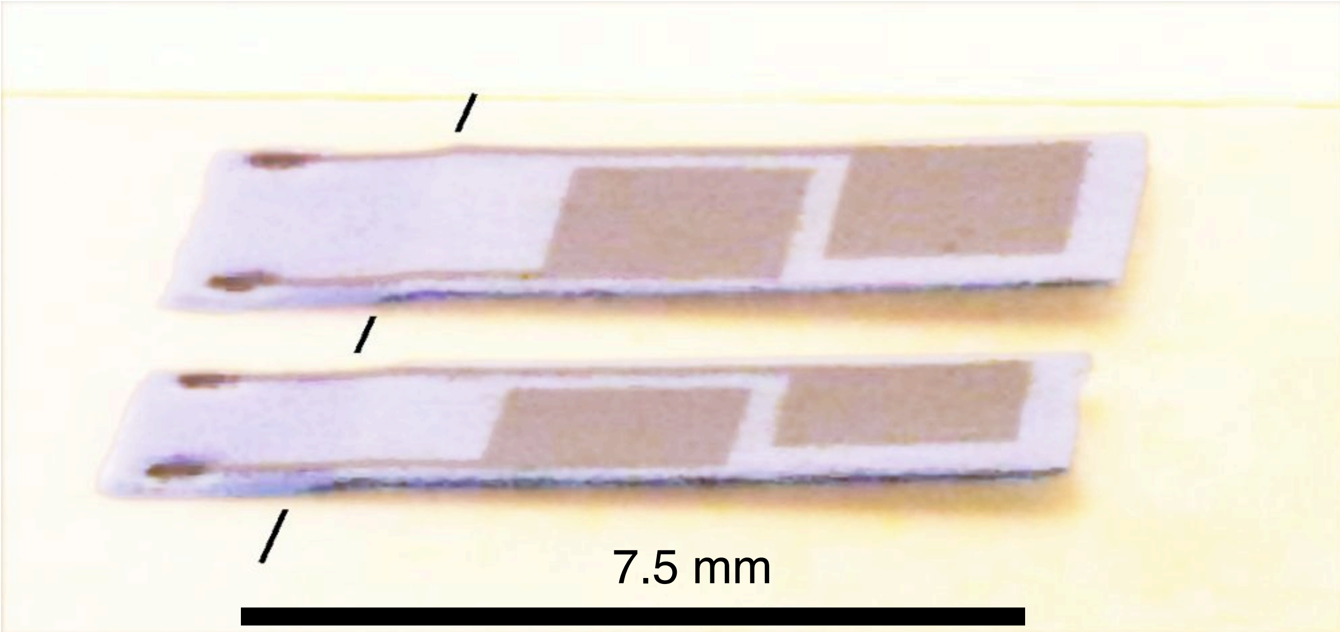
- Dip into acid (≈ 1 day) @ RT
  - MgO not very reactive
  - "Dead-burned" or additives on surface
  - 10% phosphoric or acetic acid not optimised
- Rinse with tap water
- Neutralise acid with TRIS buffer
- Rinse with deionised water
- Rinse with isopropanol
- Dry @ 60°C in oven

4. Obtained structures: cantilevers



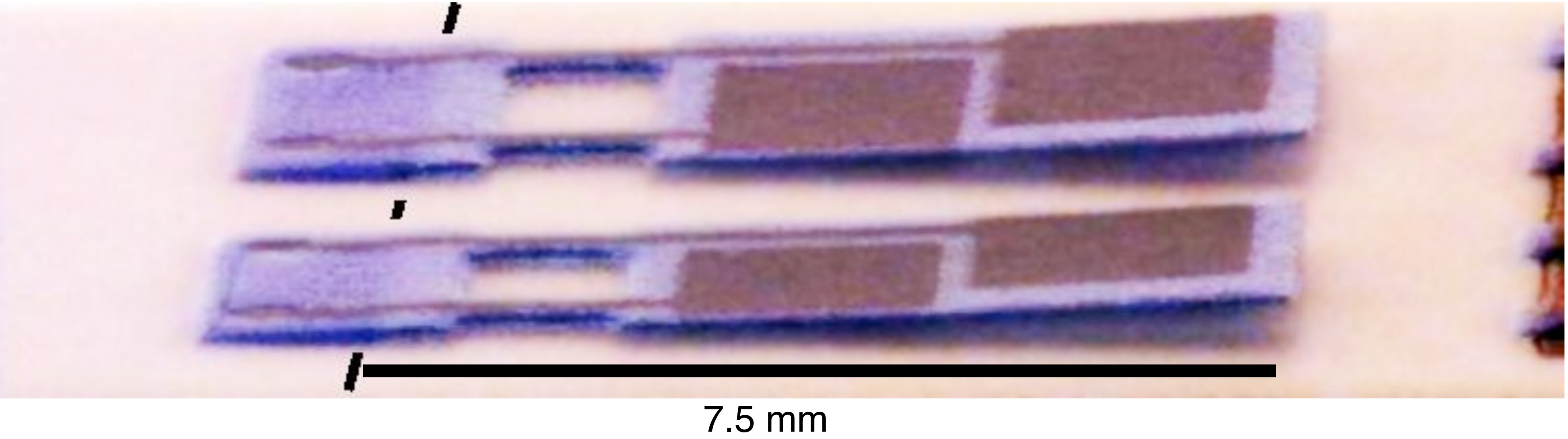
- Plain cantilever : 2 x ESL 4913 + 1 x AgPd ESL 9635B
- Lifting due to built-in strain (TCE mismatch)
  - No lifting was present before etching

4. Obtained structures: cantilevers



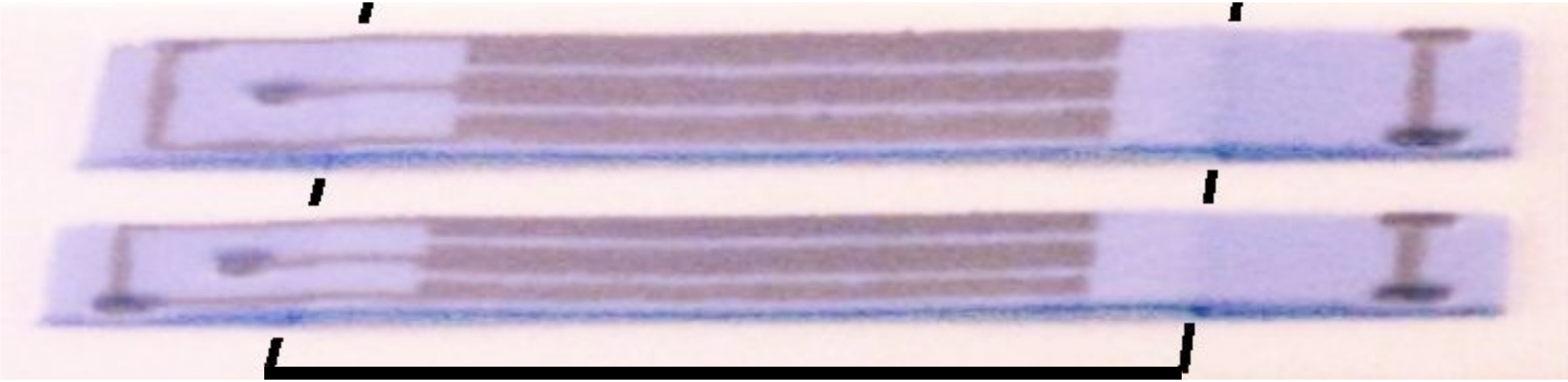
- Plain cantilever: 3 x ESL 4904 + 1 x 9535B + 1 x 4904
- Lower lifting due to partial structure compensation

4. Obtained structures: cantilevers



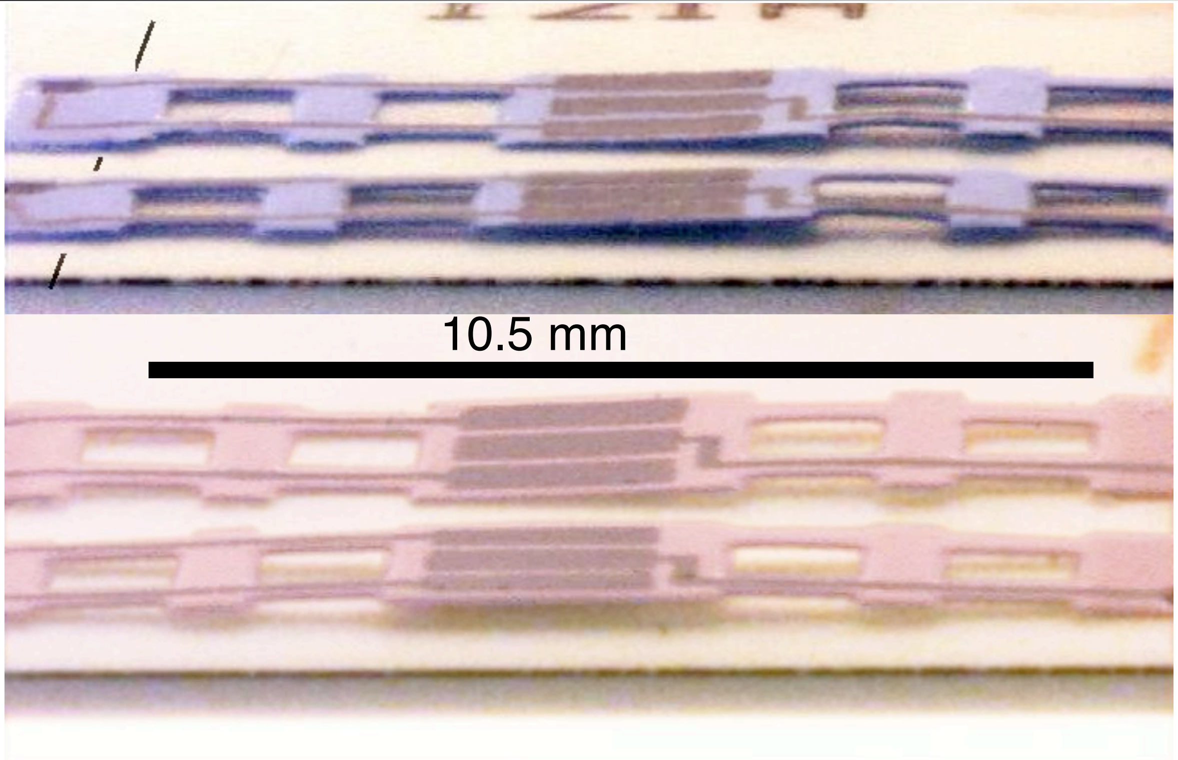
- Structured cantilever: "hinges" to increase flexibility
- Advantage: move weak point away from base-cantilever junction

4. Obtained structures: bridges



- Plain bridge: 3 x ESL 4904 + 1 x 9535B + 1 x 4904
- Other issue for bridges: buckling downward
- Most dielectrics adjusted in compression on alumina

4. Obtained structures: bridges



- 3 x ESL 4904 +
  1 x ESL 9635B +
  1 x ESL 4904
- 3 x ESL 4903 +
  1 x ESL 9635B +
  1 x ESL 4903

- Very slender structures, yet reliable fabrication
- Confirms buckling issue - bistable mechanical behaviour

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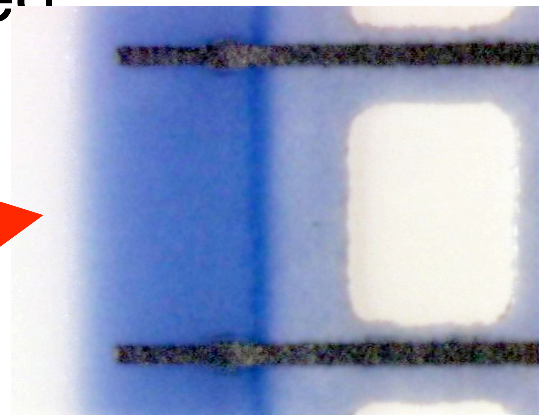
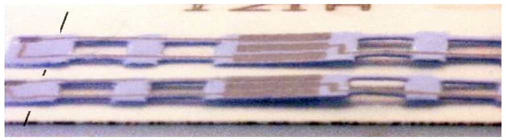
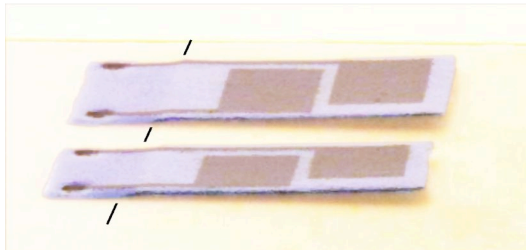
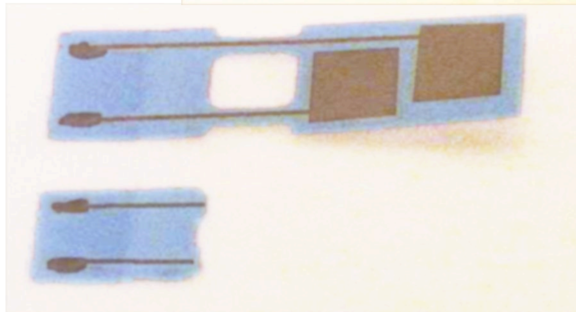
5. Conclusions

- Quite straightforward process achieved
  - MgO-based sacrificial layer
  - Standard firing sequence
- Excellent shape stability
  - Cohesion of MSP
    - No lateral contraction
    - No curling
- Issues
  - Acid etching
  - Stresses (TCE) - buckling & bending
  - Drying - capillar forces









5. Outlook

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- Solve remaining issues
  - Better MgO bonding with less additive : coating the particles
  - Optimise MSP / etching conditions (more benign)
  - Thermal stress compensation / decrease
    - Optimise structure and materials
  - Drying by sublimation if needed
    - Freeze drying (water, cyclohexanol, …)
- Functional testing of structures
  - Very sensitive force sensors + actuators, …
- Adapt to LTCC

Merci

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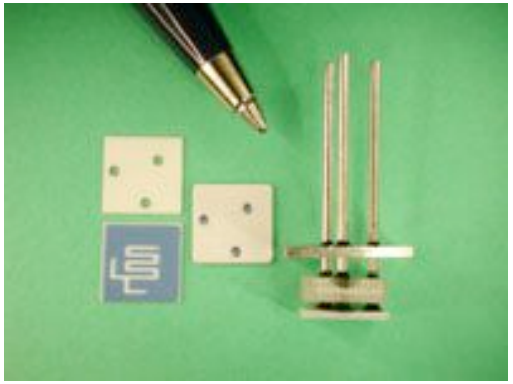
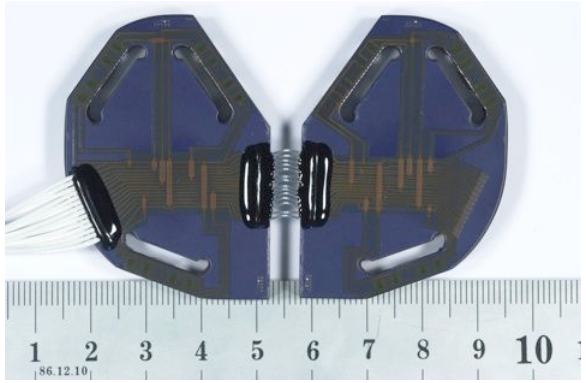
FÉDÉRALE DE LAUSANNE





Thank you !