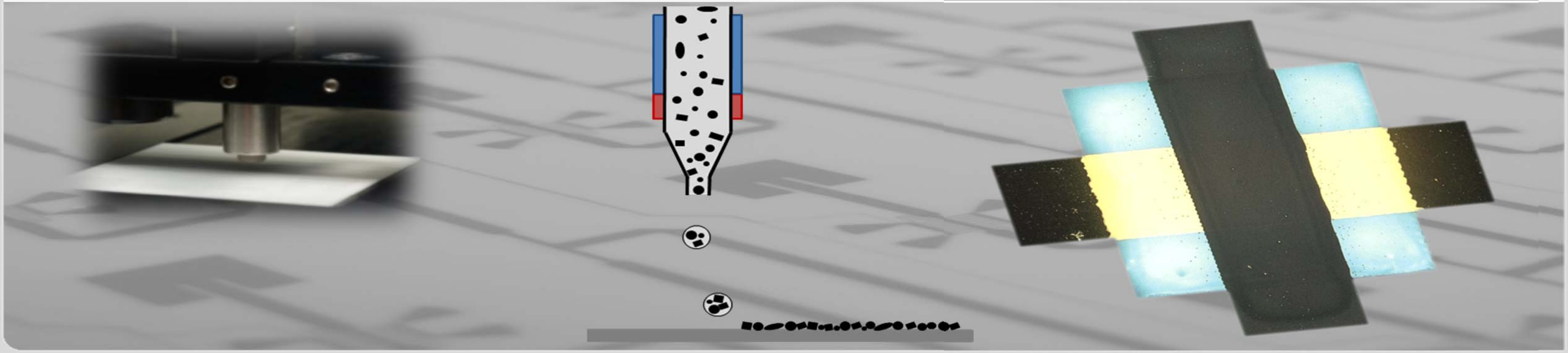
Polymerizable ceramic ink system for thin inkjet printed dielectric layers

Timo Reinheimer

Institute for Applied Materials – Energy Storage Systems (IAM-ESS)



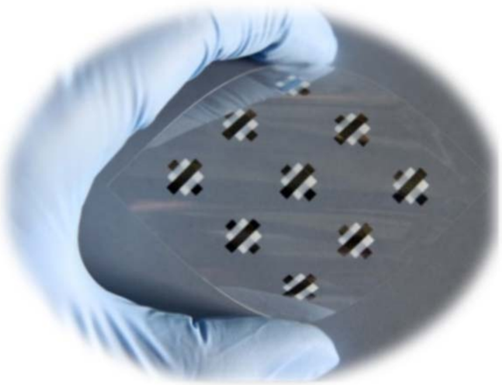
Outline

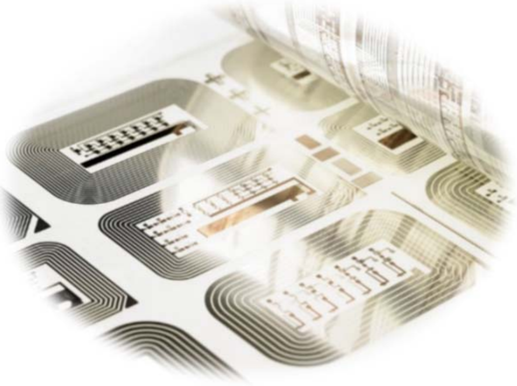
1) Capacitors

2) Printed capacitors: state of the art

3) Polymerizable ceramic ink system
   - Concept
   - Synthesis and ink development
   - Drying behavior

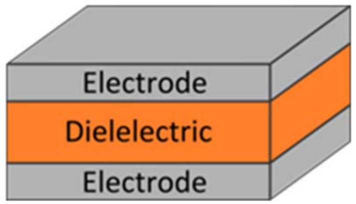
4) Dielectric properties of printed capacitors





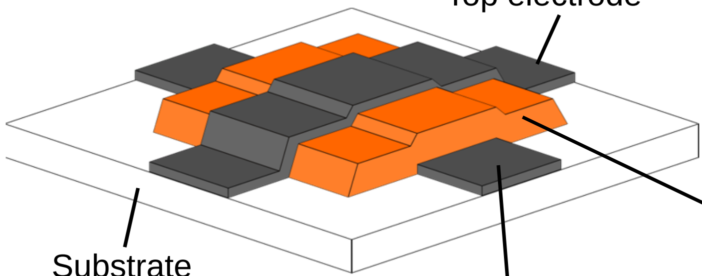
Capacitors

- **Plate-capacitors**
  - Store electrical energy
  - Simple fabrication
  - Dielectric significantly influences properties
    - Ceramic materials
    - Plastic films



$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

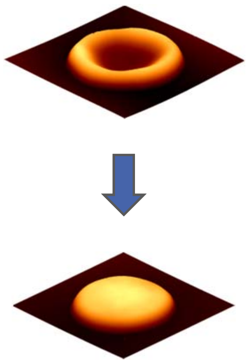
- **Fully printed MIM-capacitors**
  - Electrodes: metal
    → Commercially Ag-Inks
  - Dielectric: insulator
    → Ceramics/polymers
  - Printable substrate
    → Ceramics/polymers



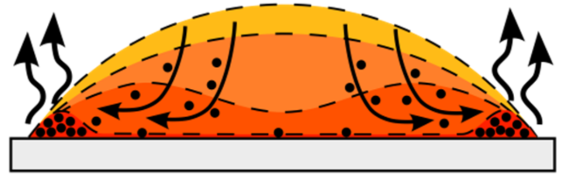
State of the art

First Author	Dielectric material	Ratio [vol%] (cer./pol.)	Substrate	Layer thickness [µm]	Permittivity	Capacity [pF/mm²]	Sintering Temperature [°C]
Kaydanova[1]	BST		magnesia	0.42	1000	21100	1100
Graddage[2]	PVP		PET	0.07	3.9	200	130
Mikolajek[3]	BST + PMMA	66.6/33.3	PET	6	42	58	120

- **How to get thinner ceramic/polymer layers with high ε_r on PET ?**
  - Challenge: drying effects lead to short circuits
- **Avoiding coffee stain effect?**
  - Homogenous topographies
  - No short circuits



coffee stain effect

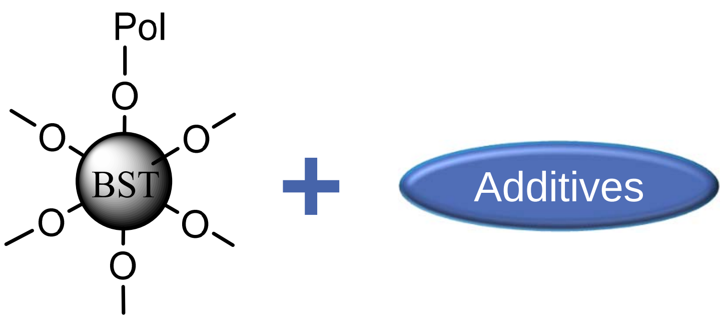


[1] T. Kaydanova et al., *Thin Solid Films* **2007**, *515*, 3820.
[2] N. Graddage et al., *Org. Electron.* **2016**, *29*, 114.
[3] M. Mikolajek, *Dissertation* **2018**.

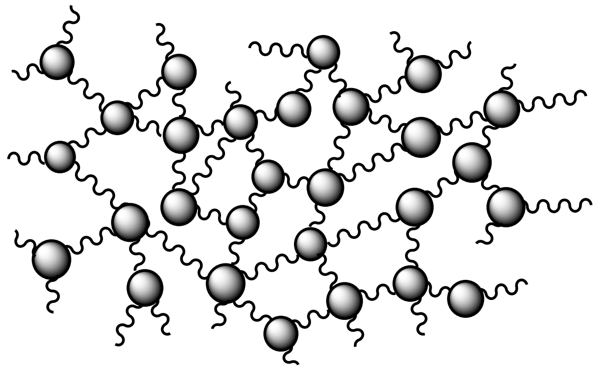
New concept: polymerizable ceramic ink system

- **Surface modified ceramic particles**
  - Introducing of a polymerizable group
  - Crosslinking during printing → strong rise of viscosity
  - Very homogenous topographies even at low layer thicknesses

Polymerizable ceramic ink



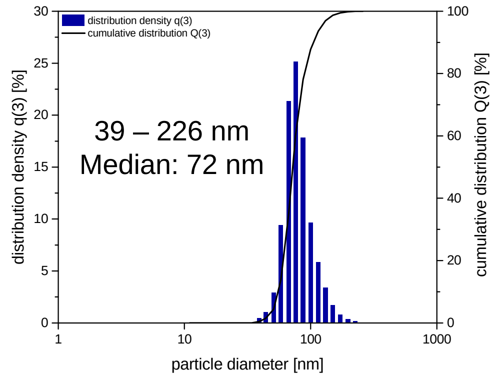
Printed particle network structure



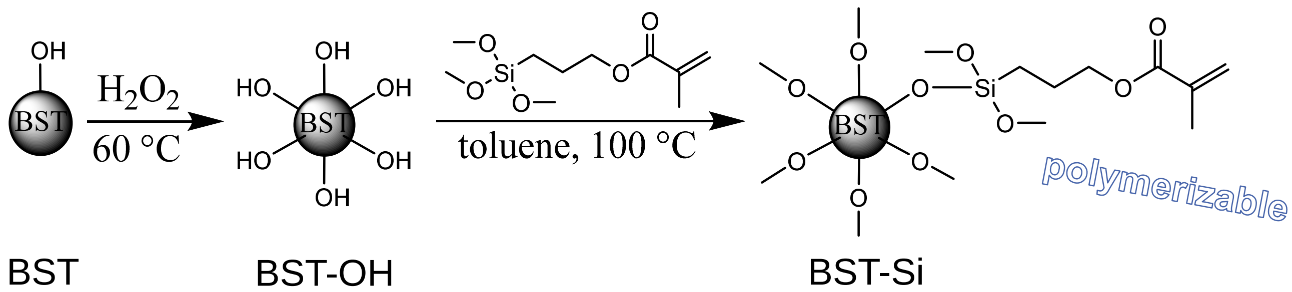
→ Control of coffee stain effect

Ceramic synthesis and surface modification

- **BST-Synthesis ($Ba_{0.6}Sr_{0.4}TiO_3$)**
  - Sol-Gel-Synthesis with acetic acid
  - Spray drying
  - Calcination at 1100 °C
  - Milling and production of the dispersion in a stirred media mill



- **Reproducible 2-step surface modification**
  - Oxidation with H_2O_2
  - Silanization with TMSPMA



→ *Analytics: thermogravimetric analysis and XPS*

Ink development

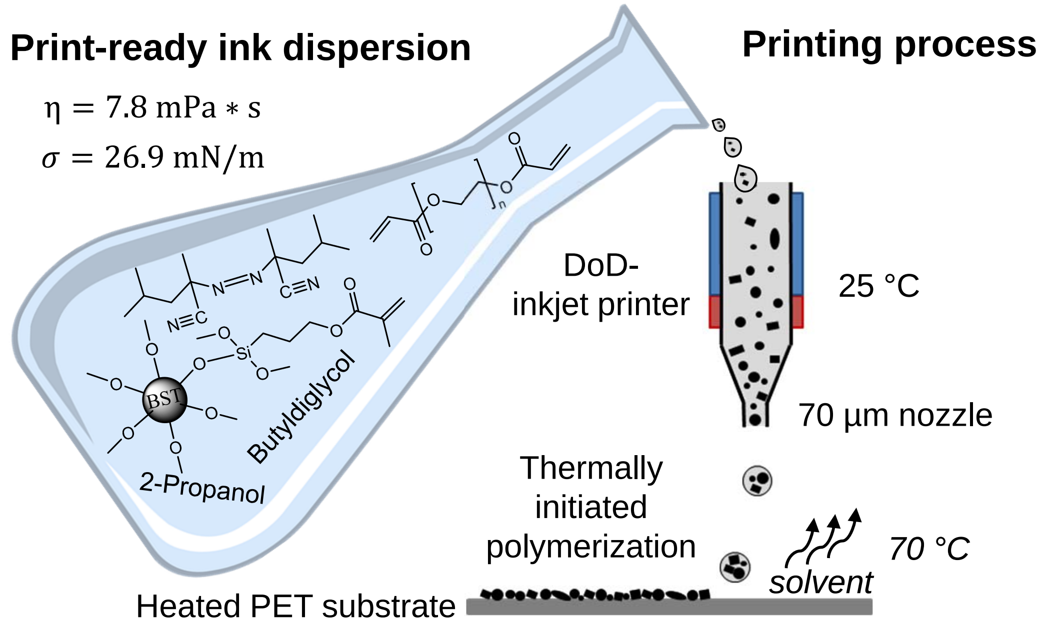
- **Ceramic powder dispersion**
  - After synthesis: powder gets dispersed in stirred media mill (deagglomeration)
    → BST-Si-Dispersion in butyldiglycol

+

Additives

+ PEG-DA (M_n:700)
+ Thermal azo-initiator
+ IPA/BDG (dilution)

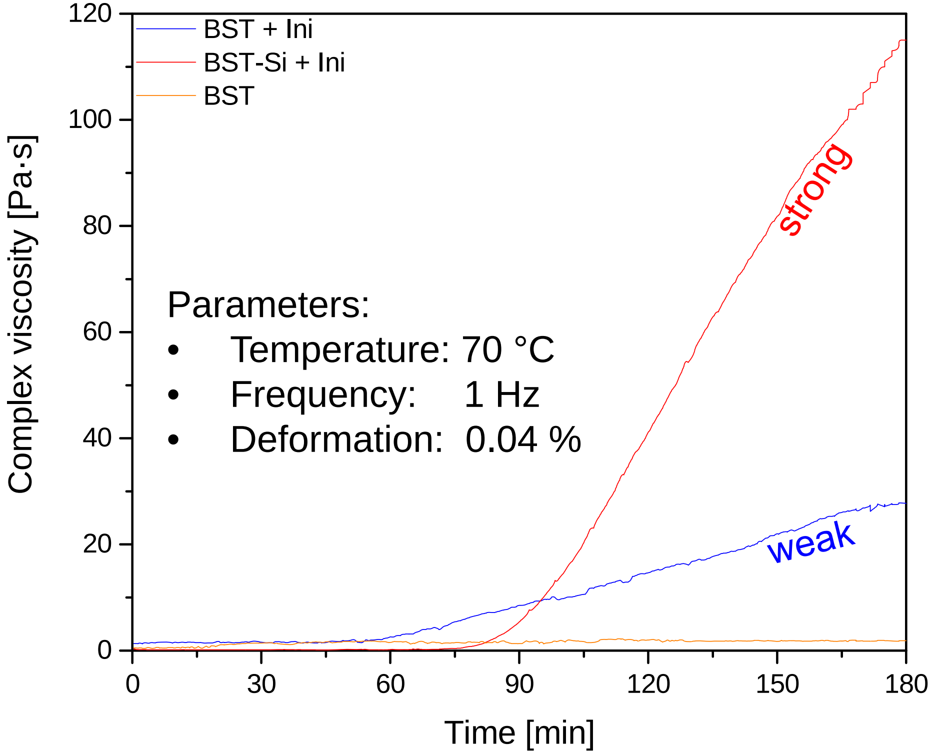
→ 10 vol% BST-Si/PEG-DA (50:50)



- **Polymerization?**
  → Oscillation measurement

Oscillation measurement

- **Surface modificated vs. non-surface modificated**
  - BST-Si with initiator vs. BST with and without initiator



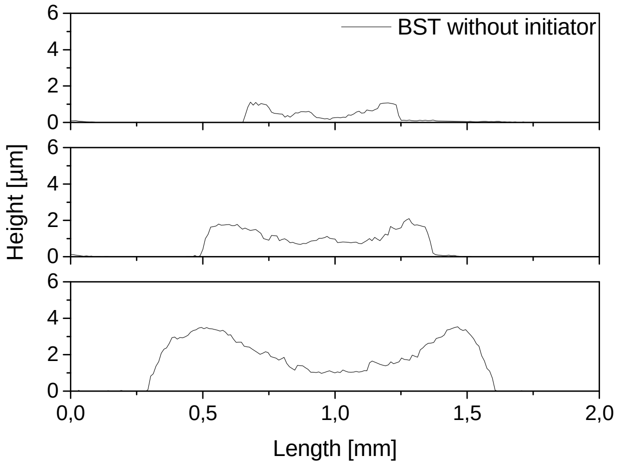
- Strong:
  → Particle network building
- Weak:
  → Polymerization of crosslinking agent
- No polymerization

Drying behavior

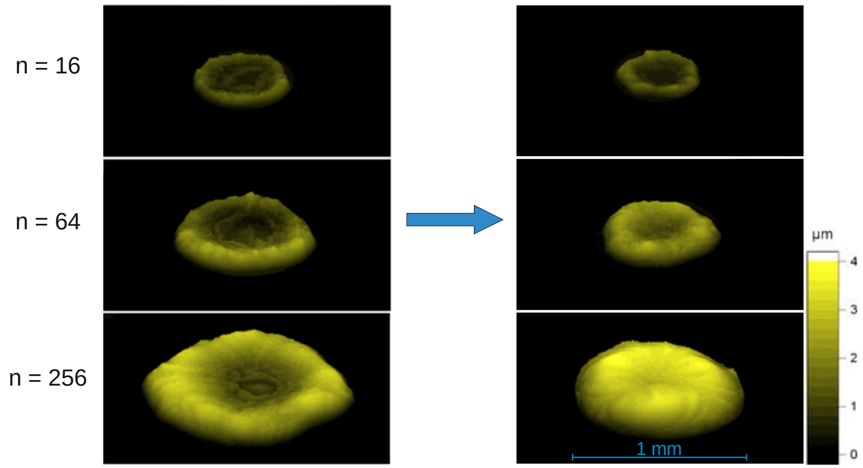
3D-Topographies of printed drops

(consisting of n droplets)

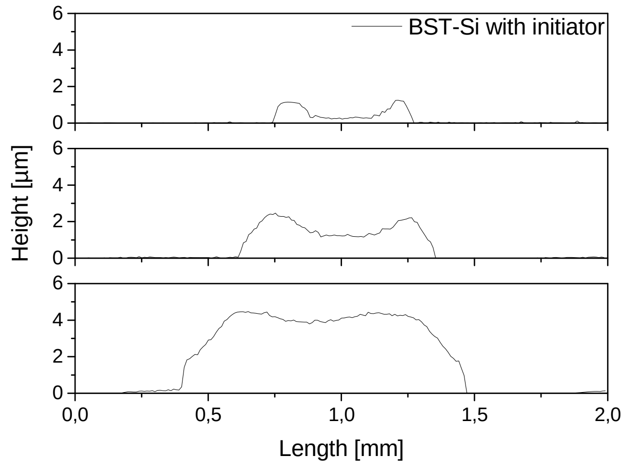
Concave, with defects



Non-surface modificated **Surface modificated**

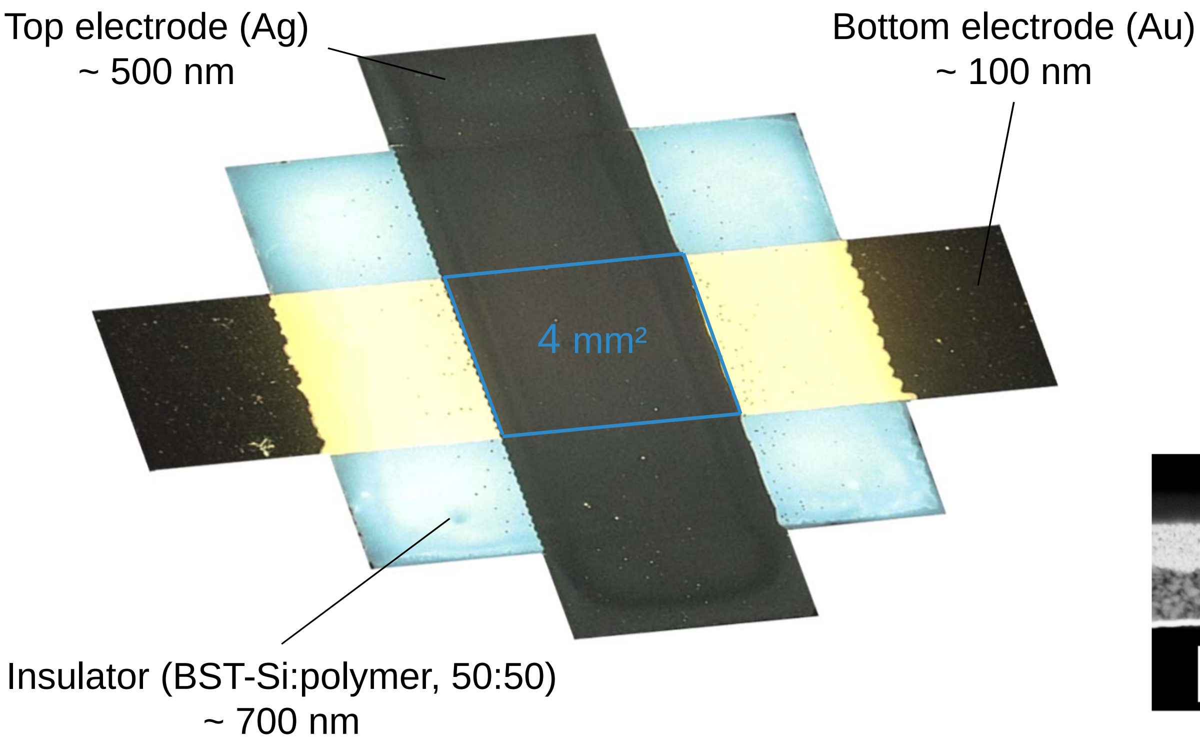


More flat, without defects



Printed capacitor

Microscope image of printed capacitor

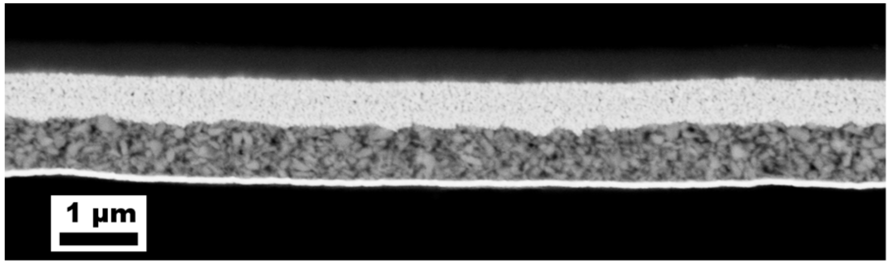


Dielectric properties

- Effective area: 4 mm²
- Capacity: ~ 2 nF
- Permittivity: ~ 41
- Q factor: ~ 17

(Capacity, Permittivity, Q factor: @ 200 kHz)

Cross sectional SEM-image



This work was supported by grants from the Deutsche Forschungsgemeinschaft (BI 1636/1-3). Thank you!

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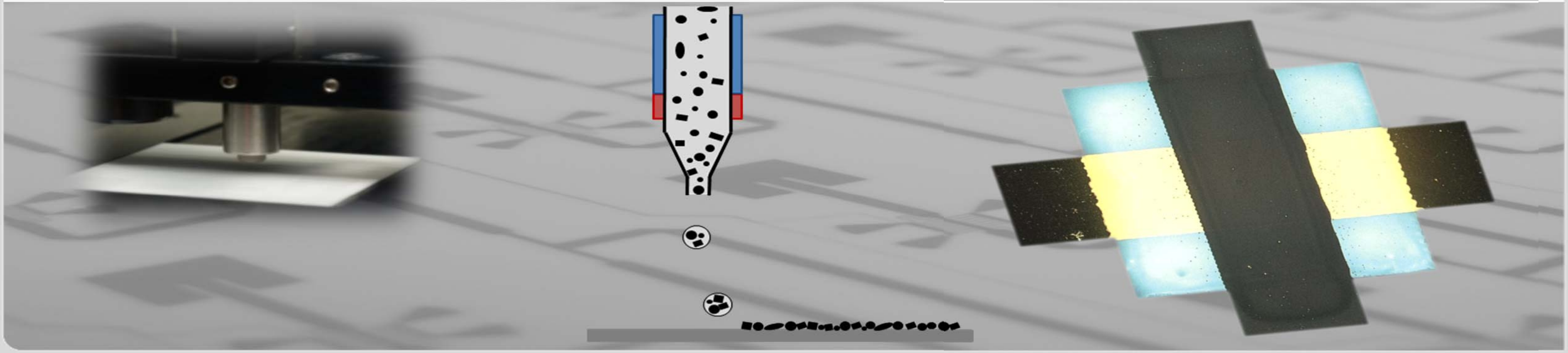
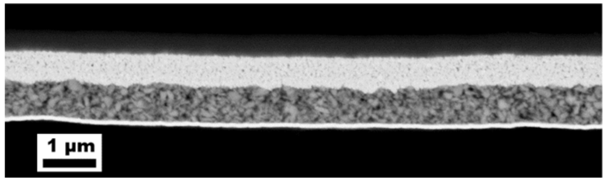


Variation of layer thickness

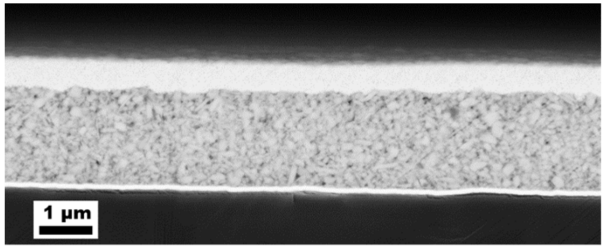
- **Options:**
  - Change drop distance
  - Multilayer printing (90 µm drop distance):

1-layer: 700 nm



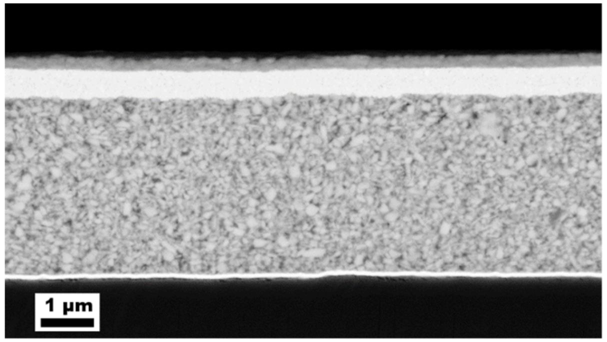
- Capacity: ~ 2080 pF
- Permittivity: ~ 41
- Q factor: ~ 17

2-layers: 1.8 µm



- Capacity: ~ 810 pF
- Permittivity: ~ 41
- Q factor: ~ 17

3-layers: 3.3 µm

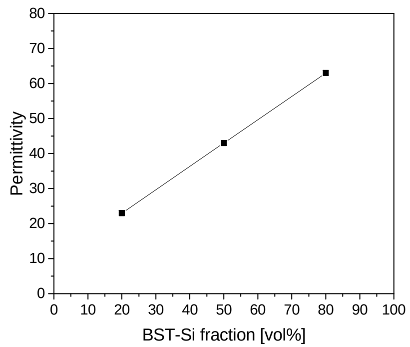


- Capacity: ~ 450 pF
- Permittivity: ~ 42
- Q factor: ~ 20

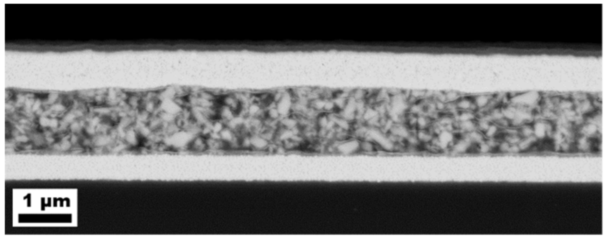
→ Permittivity remains the same ✓

Variation of BST-Si:Polymer ratio

- **Overall solid content is 10 vol% for all inks**
  - Drop distance: 70 µm
  - Bottom electrode: silver

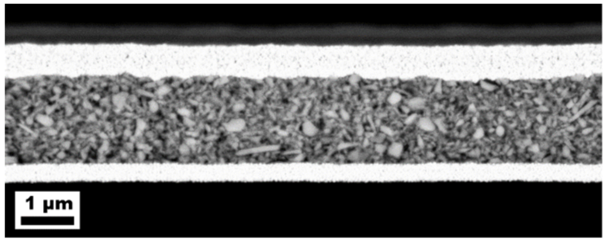


BST-Si:Polymer 20:80



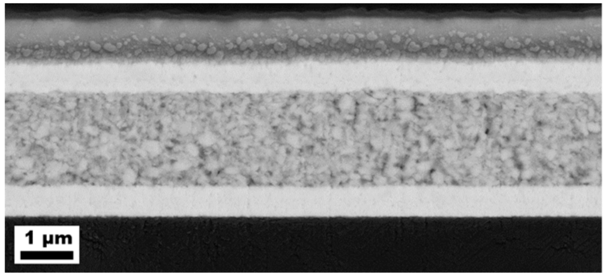
- Capacity: ~ 680 pF
- Permittivity: ~ 23
- Thickness: 1.2 µm
- Q factor: ~ 11

BST-Si:Polymer 50:50



- Capacity: ~ 950 pF
- Permittivity: ~ 43
- Thickness: 1.6 µm
- Q factor: ~ 14

BST-Si:Polymer 80:20



- Capacity: ~ 1240 pF
- Permittivity: ~ 63
- Thickness: 1.8 µm
- Q factor: ~ 14

Karlsruhe Institute of Technology

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