Polymerizable ceramic ink system for thin inkjet printed dielectric layers

Timo Reinheimer

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

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

\[ C = \varepsilon_0 \varepsilon_r \frac{A}{d} \]
## State of the art

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

### How to get thinner ceramic/polymer layers with high \(\varepsilon_r\) on PET?
- Challenge: drying effects lead to short circuits

### Avoiding coffee stain effect?
- Homogenous topographies
- No short circuits

---

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**

```
+ Additives
```

**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

\[ \text{BST} \xrightarrow{H_2O_2, 60°C} \text{BST-OH} \xrightarrow{\text{toluene, 100°C}} \text{BST-Si} \]

→ 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 (Mₚ:700)
  + Thermal azo-initiator
  + IPA/BDG (dilution)

  → 10 vol% BST-Si/PEG-DA (50:50)

- Polymerization?
  → Oscillation measurement
Oscillation measurement

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

Parameters:
- Temperature: 70 °C
- Frequency: 1 Hz
- Deformation: 0.04%

- **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 modified

Surface modified

More flat, without defects

BST without initiator

BST-Si with initiator

n = 16

n = 64

n = 256

Concave, with defects

Non-surface modified

Surface modified

More flat, without defects
Printed capacitor

Microscope image of printed capacitor

- Top electrode (Ag) ~ 500 nm
- Bottom electrode (Au) ~ 100 nm
- Insulator (BST-Si:polymer, 50:50) ~ 700 nm

Dielectric properties

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

@ 200 kHz

Cross sectional SEM-image
Polymerizable ceramic ink system for thin inkjet printed dielectric layers

Timo Reinheimer

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
Polymerizable ceramic ink system for thin inkjet printed dielectric layers

Timo Reinheimer


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

Thank you!