Development of Biodegradable Electronic Components using Printing Technologies

Fraunhofer Symposium Sendai

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2. Materials & Methods
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MOTIVATION
Printing of Biodegradable Components
Motivation - Global vision - biodegradable / bio-compostable electronics

Electronic recycling or waste incineration 2019

Biodegradable and compostable electronics 2050

Change in thinking

FOTO: www.zdnet.com

FOTO: Bodo Butz, mein-schoener-garten
Application - Biocompatible / Biodegradable electronics and materials

- Implantable Devices for surveillance of human body
- Packaging of Electronic systems for use in harsh environments
- Autarkic Sensor networks
- Food Chain and Process Chain Monitoring

Fraunhofer ENAS BIO-SMART SYSTEMS

- Human and animal welfare
- Ecological cultivation
- Sustainability
- Environment protection
- Product chains
- Consumer protection
Procedure - Printing of biodegradable electronic Components

Goal
• Environmental responsible / biodegradable (absorbable) electronics

Approach
• Substitution of conventional materials used in electronic devices by biocompatible and/or biodegradable materials

Constraint
• Properties / Performance of biomaterials and interplay with typical manufacturing technologies for electronic components

Benefit of printing
• Synergetic effects by printing technologies with additive electronic manufacturing due to flexibility, scalability, variability
Definition of terms

Diversity of biocompatible / biodegradable materials

Biodegradation

- Biodegradation is the breakdown of organic matter by microorganisms, such as bacteria, enzymes and fungi

- EN 13432: More than 90% converts within 180 days to
  - Methane, H₂O, CO₂, energy and biomass
    - Under defined temperature, humidity in the absence of free oxygen → Anaerobic
  - H₂O, CO₂, energy and biomass
    - Under defined temperature, humidity only in the presence of oxygen within 180 days → Aerobic

Biocompatibility

- "The quality of not having toxic or injurious effects on biological systems
- sustainable, mutual co-existence of biomaterials and tissues

Figure 1a: Diversity of degradable materials [1]

Figure 1b: Global market (1.4 mil. t.) of bio-based/non-biodegradable (green) and biodegradable (grey) plastics in 2012 [1]

Literature - Applications of biodegradable electronics

Biodegradable OFET

- Irimia-Vladu et al. (2011)
  - Review-like discussion about “unusual” materials in organic electronics

Translucent Printed Circuit Boards

- Hwang et al. (2012)
  - Platform with transistors, diodes, resistors, capacitors, interconnects and dielectrics

Left: Platform with transient electronics, Right: Chemical reaction of system with wafer

- Conductor
  - Magnesium (PVD)
- Dielectrics
  - Magnesium oxide, silicon dioxide (PVD)
- Semiconductors
  - Silicon nanomembranes (transfer print)
- Substrate / Packaging
  - Silk (solution casting)

# Examples of Bio-Materials for electronic Components

<table>
<thead>
<tr>
<th></th>
<th>Conductors</th>
<th>Semi- conductors</th>
<th>Dielectrics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conductors</strong></td>
<td>Inorganic</td>
<td>bio-compatible</td>
<td>bio-compatible</td>
</tr>
<tr>
<td></td>
<td>bio-degradable</td>
<td>Gold, Titanium</td>
<td>Magnesium, Zinc</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>bio-compatible</td>
<td>Pedot: PSS, Polyaniline</td>
</tr>
<tr>
<td></td>
<td>bio-degradable</td>
<td>Polypyrrole / poly(e-caprolactone)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inorganic</td>
<td>bio-compatible</td>
<td>Silicium-Carbide</td>
</tr>
<tr>
<td></td>
<td>bio-degradable</td>
<td>Zinc Oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>bio-compatible</td>
<td>Pentacene, Graphene</td>
</tr>
<tr>
<td></td>
<td>bio-degradable</td>
<td>Beta-Carotin (p-type), Indigo (n-type)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inorganic</td>
<td>bio-compatible</td>
<td>Magnesium Oxide</td>
</tr>
<tr>
<td></td>
<td>bio-degradable</td>
<td>and bio-degradable</td>
<td>Zinc Oxide</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>bio-degradable</td>
<td>PVA, Glucose</td>
</tr>
<tr>
<td></td>
<td>bio-compatible</td>
<td>Parylene</td>
<td></td>
</tr>
</tbody>
</table>
METHODS & MATERIALS

Printing of Biodegradable Components
Printing of biodegradable electronic components

Innovative additive material transfer by printing to fabricate electronics

- **Modern printing technologies**
  - ENAS utilizes printing technologies for additive manufacturing of sensors, batteries and antennas

- **Integration of biocompatible / biodegradable materials by printing**
  - Inkjet
  - Aerosol Jet
  - Stencil- / Screen Printing

Screen printed Humidity Sensor
Screen printed flexible battery with integrated printed button and LEDs
Screen printed flexible antenna
Methods & Materials
Printing Systems Inkjet

FUJIFILM DIMATIX Family

- Modern Inkjet printing Systems
  - Drop-on-Demand Piezo-Inkjet systems DMP 2831, DMP3000
  - Standard-Printheads DMC 11610 (Orifice: d=21.5 µm)
  - Printing frequencies 1-10 kHz
  - Used drop distance = 5-150 µm

Pattern morphology: lateral 20 µm – 200 µm [Single Nozzle]
vertical 500 nm – 2 µm [Single Layer]

Fujifilm Dimatix DMP 3000
Methods & Materials
Printing System Aerosol Jet

- OPTOMEC AJ300C System
  - 300 x 300 mm x-y-Vacuum stage
  - Print Speed: max. 200 mm/s
  - 2 Atomizer systems
    - Pneumatic Atomizer [1cP – 1000cP, 15ml fluid]
    - Ultrasonic Atomizer [1cP – 5cP, 1ml fluid]
  - Aerosol-, Ink- and substrate heater
  - Fine feature print head [min. line width 10 µm]
  - Laser-Curing-System [IR Laser, 700 mW, 830 nm]
  - Material in-flight mixing option

Pattern morphology: lateral 10 µm – 200 µm [Single Nozzle]
vertical 500 nm – 2 µm [Single Layer]
Methods & Materials
Screen and stencil printing on wafer level

Equipment DEK Horizon 03iX
- Screen frame: 736 x 736mm
- Printable area: 510mm x 508.5mm
- Additional technology modules
  - Module for via filling (a)
  - Module for dispensing (b)
  - Vector guard stencil printing
- Machine alignment >2 Cpk @ +/- 12.5μm, 6 Sigma
Methods & Materials
Systematics of printing functional materials

Technological triangle of functional printing
- Interplay of three cornerstones for material deposition
Methods & Materials

Systematics of printing functional materials

Technological triangle of functional printing
- Application defining and cornerstone cohesive properties

- **Ink**
  - Printability
  - Solidification / functionalization

- **Printing-System**
  - Repeatability + Quality

- **Substrate**
  - Wettability + mechanical / thermal stability

APPLICATIONS
Nanoparticle Bonding

Background

Nanoparticle Inks/Pastes – Post-treatment and sintering
- Suspensions of metal particles in solvents and binders
- Posttreatment for dense layer and electrical conductivity:
  - Drying out solvents, burning out organic shells, sintering

Sintering without pressure (Particle necking due to diffusion effects)
- Hot plate/oven
- Laser
- Chemical
- Intense pulsed light (IPL)
- Plasma sintering
- IR sintering

Experimental Setup
- Sintering of Ag Nanoparticles and SEM investigation at different temperature steps

Fig 5: Nanoparticle filled Ink, Drying out solvents, burning out organic shells, sintering

Fig 6: 2 Particle Model [J. I. Frenkel (1945)]

SEM Investigation - Sintering of Ag Nanoparticles and grain size at 60°C, 100°C, 200°C, 250°C, 300°C
Methods & Materials

Systematics of printing functional materials

Technological triangle of functional printing

- Starting environment for development

- Ink
  - Dielectric: cPVP
  - Conductor: Silver, Zinc
  - Semiconductor: Indigo

- Printing-System
  - Inkjet
  - Aerosol Jet
  - Screen Printing

- Substrate
  - PEN
  - PLA

Organic field effect transistor

cPVP - Polyvinylphenol
PEN - Polyethylennaphthalat
PLA - Polylactide
RESULTS

Printing of Biodegradable Components
Results - Evaluation of substrate materials

Continuously research for substrates (ongoing)

- **Main Parameter for classification** → Temperature stability
  - „unsuitable“
  - “fit for limited duties”
  - “unconditionally suitable”

- **Example for biodegradable substrate**
  - TAGHLEEF Industries: Polylactide (PLA) Foils, Series « NATIVIA», different thickness available

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 °C</td>
</tr>
<tr>
<td>NTSS 25 µm</td>
<td>Stable</td>
</tr>
</tbody>
</table>

- **Additional printing related surface properties**
  - Roughness, free surface energy, chemical resistance / compatibility to ink system, coefficient of thermal expansion (CTE)
Results - Evaluation of substrate materials

Substrate dependent process evaluation with reference conductive materials

- STEP 1: Printing and drying of nano particle based silver inks onto biodegradable PLA
  - Development of stable Inkjet printing process of large area patterns

- Reason for deformation: temperature and drying driven tensions between printed layer and substrate
  - Consequence no further printing process due to strong mechanical deformation of substrate
Results - Evaluation of substrate materials

Substrate-dependent process evaluation with reference conductive materials

- **STEP 2: Sintering of printed silver layers onto PLA**
  - Intense Pulsed Light sintering vs. IR-Laser sintering

**Ink jet, PLA, intense puls light sintering, Ag from company ANP**

**Aerosol jet, PLA, IR laser sintering (laser power constant), Ag from company Genesink**
Results - Evaluation of printable conductive materials

Process evaluation with biodegradable conductive materials

- Sintering of screen printed zinc (µm particle scale) layers onto polyimide
  - Evaluation of sheet resistance

- Resistivity to high compared to reference silver material
  - Switch to nano particle based system
    - Reduced energy input for sintering temperature sensitive biodegradable substrates
    - Reduced sheet resistance by testing of alternative sintering setup ups (i.e. Laser)
Results - Printing of biodegradable electronic components

Inkjet printed Organic Field Effect Transistor (OFET)

- Successive substitution of functional layers with biodegradable materials
  - OFET-Built up: BGBC (Bottom Gate Bottom Contact)

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Substrate</th>
<th>Electrode Gate</th>
<th>Dielectric</th>
<th>Electrode Source-Drain</th>
<th>Semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - Swapped Semiconductor (Bio-degradable)</td>
<td>PEN</td>
<td>Ag</td>
<td>cPVP</td>
<td>Ag</td>
<td>Indigo</td>
</tr>
</tbody>
</table>

## Results - Printing of biodegradable electronic components

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Substrate</th>
<th>Electrode</th>
<th>Dielectric</th>
<th>Semiconductor</th>
<th>W / L Ratio</th>
<th>Saturation</th>
<th>Max. Channel Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - <strong>Dielectric</strong> (Bio-degradable)</td>
<td>PEN</td>
<td>Ag</td>
<td>cPVP</td>
<td><strong>Indigo</strong> (n-type)</td>
<td>360 (18 / 0.05) mm</td>
<td>0 – 20 V</td>
<td>3.5 mA</td>
</tr>
</tbody>
</table>

### Table

- **Dielectric**: PEN Ag | cPVP
- **Semiconductor**: PEN Ag | cPVP
- **W / L Ratio**: 360 (18 / 0.05) mm
- **Saturation**: 0 – 20 V
- **Max. Channel Current**: 3.5 mA
CONCLUSION AND OUTLOOK

Printing of Biodegradable Components
Conclusion and Outlook

- Successfully printed substitution of functional layers with biodegradable materials
- Zinc as conductor, PLA as substrate and Indigo as semiconductor can be used
- The post-treatment (energy level) plays an important role for the material integration

**Ink / Substrate / Multi-Layer interaction**
- Continuous testing/manufacturing of ink and substrate materials
- Characterizing material dependent performance for biodegradable devices
- Research for new and selfmade printable and processable ink recipes

**Variation of process parameters**
- Sintering / post treatment
- Printing technologies
- Device layout / design
- Multi-layer built up

**Hybrid Manufacturing**
- Combination of printing technologies with other approaches for additive material transfer, i.e.: CVD, PVD, Spin coating...

**Applications**
- Biodegradable Sensors
- Biodegradable OFET
- Biodegradable Circuitry
- Human / Veterinary Medicine
- Agriculture
- Environmental monitoring

Testing of device performance vs. Biocompatibility / degradability
Festive ceremony on December 17, 2018 – signing continuative contract of Fraunhofer Project Center
Fraunhofer Project center MEMS/NEMS devices at Tohoku University

- Acoustic MEMS (micro speaker, microphone)
- High strength thin film metallic glass
- Magnetostrictive, amorphous metal
- Thermoelectric materials
- Biodegradable materials
Thank you very much for your attention

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