Low Temperature Sintering of PZT

Anna Medesi
Albert-Ludwigs-University of Freiburg
Department of Microsystems Engineering (IMTEK)

Laboratory for Material Process Technology
Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3}

- Solid solution of PbZrO\textsubscript{3} and PbTiO\textsubscript{3}
- Ferroelectric functional ceramic
- Properties sensitive to Zr/Ti ratio
- Largest electromechanical coupling factor at the MPB: Zr / Ti = 52 / 48
Application using PZT films

**Actuators**
- Micromotors
- Micropumps

**Sensors**
- Displacement sensors
- Proximity sensors
- Pressure sensors
- Force sensors

**Capacitors**
- Ferroelectric RAMs

**Transducers**
- Lamb wave pumps
- Energy harvesters

*PICMA Stack Actuator (PI Ceramic GmbH)*

*Pressure Sensor (SINTEF, Norway)*

*FeRAM Device (Fujitsu Semiconductor Europe)*

*Energy Harvester V25W (Mide Technology Corporation)*
Fabrication of PZT films

Thin films < 3µm
- Deposition on glass/silicon/metal substrates
- CSD, CVD, PLD, Sputtering, EPD

Thick films > 50 µm
- No need for a substrate
- Tape casting method

MULTILAYER PIEZOELECTRIC BENDING TRANSDUCER

C. Eichhorn, 2011
Ceramic Multilayer Technology

NEW: Piezoelectric Multilayer with Ag-Electrodes
Challenge: Material Compatibility

\[ T_{\text{SINTER}} (\text{PZT}) \approx 1200 \degree \text{C} \]

\[ T_m (\text{Ag}) = 961 \degree \text{C} \]

PZT-ML are fabricated with high temperature stable inner electrodes from Pt or Ag/Pd alloys.

Ag can not be cofired together with PZT

Low Temperature Co-fired Piezo Ceramic

Metall prices [US-$/oz]

|   |   |
|---|---|
| Ag | 14.77 |
| Pd | 703.87 |
| Pt | 1,100.81 |

Source: finanzen.net, 18.11.2014
Further Benefits of PZT-based LTCC

| MATERIAL COMPATIBILITY | STABILIZATION OF ELECTROMECH. PROP. | REDUCTION OF PROCESS COSTS |
|------------------------|-------------------------------------|---------------------------|
| Co-firing of Hybrid ML structures with integrated LTCC-Layers | Reduction of evaporation of volatile PbO out of PZT during the sintering process, so that the subsequent piezoelectric components become more reliable | Less environmental pollution through less evaporation of Pb-compounds Less energy consumption through lowered sintering temperatures |
Approaches for Lowering the $T_{SINTER}$

1. Hot-pressing in oxygen
2. Vacuumed-air-venting process
3. Using fine ball-milled powders
4. Using bimodal powders
5. **Liquid Phase Sintering Technology**
1. Incorporation of low-melting **metal oxides** into the ‘green’ unsintered ceramic

2. **Formation of a liquid-phase** at temperatures about 600 to 800 °C

3. **Acceleration of densification** through facilitating the PZT particles rearrangement

4. **Formation of sintering necks** with subsequent grain growth
Commercial Ferroelectric Hard PZT

**PIC 181 (PI Ceramic)**

- Withstands high mechanical and electrical stresses
- Properties change only hardly in dynamic long-term operations
- Relatively low permittivity
- High electromechanical coupling factors
- Very low dielectric losses
- Very high mechanical quality factor

| Property          | Value   |
|-------------------|---------|
| $T_C$             | 330 °C  |
| $\varepsilon_{33}^T / \varepsilon_0$ | 1200    |
| $\varepsilon_{11}^T / \varepsilon_0$ | 1500    |
| tan $\delta$      | $< 3 \cdot 10^{-3}$ |
| $k_{31}$          | 0.33    |
| $k_{33}$          | 0.66    |
| $k_p$             | 0.56    |
| $d_{31}$          | -120 pC/N |
| $d_{33}$          | 265 pC/N |
| $Q_m$             | 2000    |

well suited for vibration energy harvesters driven in continuous use in resonance mode with only low intrinsic warming of the component
### Investigated Sintering Aids

|   | Aid:     |   |   |   |   |   |
|---|----------|---|---|---|---|---|
| 1 | Li₂CO₃   | 2 | Li₂O | 3 | Bi₂O₃ | 4 | V₂O₅ |
|   |          |   |      |   |        |   |      |
|   | Tₘ:      |   |      |   |        |   |      |
|   | 720°C    |   |      |   |        |   |      |
|   | Han et al., 2011, Korea | Lee et al., 2005, Korea | Wang et al., 1992, China | Seo et al., 2011, Korea | Corker et al., 2000, Denmark | Ahn et al., 2006, Korea |

|   | Aid:     |   |   |   |   |   |
|---|----------|---|---|---|---|---|
| 5 | MnO₂     | 6 | PbO  | 7 |       | 8 |       |
|   |          |   |      |   |        |   |      |
|   | Tₘ:      |   |      |   |        |   |      |
|   | 535°C    |   |      |   |        |   |      |
|   | CORKER et al., 2000, Denmark | Yoo et al., 2005 Japan | Lee et al., 2005, Korea | Jin et al., 2003, Korea | Wang et al., 1992, China | Seo et al., 2011, Korea |

|   | Aid:     |   |   |   |   |   |
|---|----------|---|---|---|---|---|
| 9 | Li₂CO₃ · Bi₂O₃ · CuO (1:1:4) | 10 | CuO  |  |   |   |
|   |          |   |      |   |        |   |      |
|   | Tₘ:      |   |      |   |        |   |      |
|   | 1326°C   |   |      |   |        |   |      |
|   | Corker et al., 2000, Denmark | Vötsch et al., 2007, Austria | Nielsen et al., 2002, Slovenia | Yoo et al., 2004, Korea | Wang et al., 2000, Japan | Nam et al., 2011, Korea | Lee et al., 2000, Korea |
Preparation and Characterization of 20 different PZT-Sintering Aid Combinations

... for each SA in 2 volume fractions: 2 vol.% and 5 vol.%

Microstructure
- porosity density

Piezoelectric properties
- charge constant $d_{33}$

Mechanical stability
- breaking strength $\sigma_0$

Thermal behavior
- $T_{SINTER}$
Thermal Behavior

Dilatometry:
Detection of pellet shrinkage

Source: TA Instruments

Length ↓ with T ↑

Result for the composition:
PZT + 2 vol.% Li₂CO₃

$T_{SINTER} = 814 \degree C$
Highest Densification Rate

- Green dots: 2 vol.%
- Blue dots: 5 vol.%

sintering aids

- LBCu
- Bi$_2$O$_3$
- PbO·WO$_3$
- Cu$_2$O·PbO
- PbO
- Li$_2$CO$_3$
- Li$_2$O
- CuO
- V$_2$O$_5$
- Mn$_2$O

Lowest $T_{\text{SINTER}}$: PZT + 2 vol.% LBCu

Temperature / °C
Almost 100% of the theoretical density of PZT sintered @ 1200 °C:

PZT + 5 vol.% LBCu sintered @ 900 °C
Microstructure

PZT

PZT + 5 vol.% PbO·WO₃

PZT + 5 vol.% LBCu

porous
dense @ 900 °C
**Mechanical Stability**

**Performed:**
3-point-bending tests according to DIN EN 843-1 on > 10 specimens for each PZT-SA composition

**Measured:**
Breaking strength of each specimen

\[ \sigma_f = \frac{3 \cdot F \cdot d}{2 \cdot b \cdot h^2} \]

**Evaluated:**
Characteristic breaking strengths with Weibull statistic

\[ P_V (\sigma_f) = 1 - \exp \left( - \left( \frac{\sigma_f}{\sigma_0} \right)^m \right) \]

using Maximum-Likelihood-Methode

\[ L = \prod_{j=1}^{N} \left( \frac{m}{\sigma_0} \right) \left( \frac{\sigma_{fj}}{\sigma_0} \right)^{m-1} \exp \left[ - \left( \frac{\sigma_{fj}}{\sigma_0} \right)^m \right] \]
Mechanical Stability

\[ \sigma_f \]

\[ \sigma_0 \]

failure probability

breaking strength
Mechanical Stability

Characteristic Breaking Strength

- 2 vol.%
- 5 vol.%

Most stable films:

PZT + 5 vol.% LBCu

Very brittle!
Piezoelectric Properties

**d_{33} values**

- Green circle: 2 vol.%
- Blue circle: 5 vol.%

| Sintering Aids | d_{33} (pC/N) |
|----------------|--------------|
| CuO            | 5            |
| LBCu           | 42           |
| PbO·WO₃        | 70           |
| Cu₂O·PbO       | 82           |
| Li₂CO₃         | 37           |
| V₂O₅           | 71           |
| Li₂O           | 74           |
| Bi₂O₃          | 46           |
| PbO            | 14           |
| Mn₂O           | 14           |

Nearly the piezoelectricity of PIC 181 (d_{33} = 265 pC/N) is reached:

PZT + 5 vol.% CuO
We fabricated piezoelectric ML with inner electrodes from pure Ag.

10 sintering aids for hard PZT have been investigated.

Mechanical stability, microstructure, thermal behavior, and piezoelastic properties of low temperature sintered thick films (t ≈ 100 µm) were studied.

Films made of PZT + LBCu sintered @ 900 °C shows:

a) Lowest $T_{SINTER}$ (641°C)

b) Highest density ($\rho_{rel} = 97\%$)

c) Highest mechanical stability ($\sigma_0 = 77$ MPa)

d) High piezoelectric properties ($d_{33} = 246$ pC/N)

Addition CuO has a positive effect on the piezoelectric properties of PZT.
THANK YOU
FOR
YOUR KIND ATTENTION!
Co-Casting – The New Manufacturing Process

For film thicknesses < 50 µm required green tape thicknesses: < 80 µm

Limit of accurately metallizing and stacking is reached

Co-casted piezoelectric ML with interdigital electrode structure

- Electrode thickness: 5-10 µm
- Ceramic layer thickness: 30-70 µm