PREPARATION OF $\text{BaPbO}_3$ ELECTRODE THIN FILMS
BY RF MAGNETRON SPUTTERING
AND THEIR PROPERTIES

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**Background** - Electrode materials for FeRAM & BaPbO$_3$-

**Electrode for FeRAM**

Degradation of FeRAM capacitors

**fatigue and imprint**

Electrode materials for the capacitors

- **Ir**: reduce Pb diffusion
- **IrO$_2$, RuO$_2$**: oxide
- **SrRuO$_3$**: perovskite

Barium metaplumbate

*BaPbO$_3$ (BPO)*

**Feature of BaPbO$_3$**

1. **Conductive Oxide**

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Formula</th>
<th>a, b, c (Å)</th>
<th>Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrRuO$_3$</td>
<td>Perovskite</td>
<td>a = 5.56, b = 5.55, c = 7.89</td>
<td>1 $\times$ 10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>Rutile</td>
<td>a = 4.50, c = 3.15</td>
<td>4.9 $\times$ 10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>(La,Sr)CoO$_3$</td>
<td>Perovskite</td>
<td>a = 3.81</td>
<td>&lt; 10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>BaPbO$_3$</td>
<td>Perovskite</td>
<td>a = 4.6265</td>
<td>3 $\times$ 10$^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

2. **Perovskite structure**

3. **Pb included**

- compensate for Pb defect in PZT
Objective

Reported

- Prepared by CSD (Chemical Solution Deposition method, on SiO$_2$/Si)$^{1,2}$
  - BaPbO$_3$ obtained at 550 $^\circ$C sintering
  - $\mu$: 1.6 $\times$ 10$^{-2}$ $\mu$m (SiO$_2$/Si)
    (Bulk: 3 $\times$ 10$^{-4}$ $\mu$m *)
- **Recently**, fatigue free PZT film capacitors used BPO electrode. (on SiO$_2$/Si)$^3$

XRD profile of PZT/BPO by CSD

Preparation of high quality BPO thin films

- Preparation of BaPbO$_3$ thin films by rf magnetron sputtering
  - Dependence on process and temperature
- Epitaxial growth of BaPbO$_3$
  - Al2O3, MgO substrates
- Deposition of Ba(Pb$_{1-x}$Bi$_x$)O$_3$ films
  - Low sheet resistance & preparation temperature
- Preparation of BaPbO$_3$ films by laser ablation

*2 I. Kawakami et al. IFFF 2003
Objective

- Preparation of BaPbO$_3$ thin films by rf magnetron sputtering
  - Dependence on process and temperature
  - Low sheet resistance
  - Optimized condition
  - Properties of PZT film capacitor using BaPbO$_3$

- Epitaxial growth of BaPbO$_3$
  - MgO, Al$_2$O$_3$ single crystal substrates
  - PZT/BPO epitaxial structure

- Deposition of Ba(Pb$_{1-x}$Bi$_x$)O$_3$ films
  - Dependence on Bi substitution
  - Low preparation temperature

- Preparation of BaPbO$_3$ films by laser ablation
  - Dependence on process and temperature
  - Optimized condition
  - Preparation of PZT capacitor using BaPbO$_3$ top electrode
Preparation condition of BaPbO$_3$ thin films

**This work**

- **Preparation conditions**
  - **Substrate heating**
    - **Post anneal**
    - **Substrate Temperature**
      - R.T.
      - 100 – 550 °C
    - **Input Power**
      - 100 W
    - **Deposition Pressure**
      - 10 mTorr
    - **Sputtering Gas**
      - Ar:O$_2$ = 1:1
    - **Target**
      - BaCO$_3$ : PbO = 1.0 : 1.5
    - **Deposition Time**
      - 30 min
    - **Substrate-Target Distance**
      - 40 mm
    - **Substrate**
      - SiO$_2$/Si (100)
    - **Anneal**
      - 250 – 600 °C
      - 30 min, in Air

**Reported**

- **Equipment**
  - rf magnetron sputter, SPF-210H (Anelva)

**Dependence of crystallinity of BPO films on the preparation methods.**

**Dependence of the films on post anneal & substrate temperatures.**

**Diagram:**

- **Precursor**
  - Spin coat + Dry
  - Calcination
  - Sintering (Post anneal)
- **Metal Oxide**
  - Sputtering (R.T.) + Post anneal
  - Sputtering (@RT)
- **Perovskite BPO**
  - Sputtering

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This work

Reported
**XRD profiles of BaPbO$_3$ thin films**

- **Post annealing**: 400 $^\circ$C - 650 $^\circ$C
- **Substrate heating**: 350 $^\circ$C - 550 $^\circ$C

BPO thin films were prepared at low temperature:

- 550 $^\circ$C (CSD) $\rightarrow$ 350 $^\circ$C (Sputtering)
Sheet resistance of BaPbO$_3$ thin films

Resistivity: four probe method
- Probe head (K504RB, Kyowariken)
- Space between terminals: 1 mm
- Terminals R: 150 $\mu$m
- Materials: WC

Perovskite BaPbO$_3$ thin films have low resistivity
$2.5 \times 10^{-3} \sim 2 \times 10^{-1}$ $\Omega \cdot$ cm
Fabrication of PZT/BPO capacitor

<table>
<thead>
<tr>
<th>Structure</th>
<th>$2P_r$ (C/cm$^2$)</th>
<th>$2E_c$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/PZT/Pt</td>
<td>53.1</td>
<td>166</td>
</tr>
<tr>
<td>BPO/PZT/Pt</td>
<td>55.7</td>
<td>215</td>
</tr>
<tr>
<td>Pt/PZT/BPO</td>
<td>74.7</td>
<td>233</td>
</tr>
</tbody>
</table>
Adhesion of $\text{BaPbO}_3$ films

Annealing after deposition PZT films (600 $^\circ$C, 30 min)

Peeling off BPO films from substrates

Improvement of the adhesion

Films surface after annealing
Fatigue performance of PZT capacitors with various electrodes

- Fatigue was slightly reduced by BPO top electrode.
- Crystallinity of PZT films for BPO electrodes
- Optimum preparation condition of PZT on BPO is different from that of Pt

Improvement for crystallinity of PZT thin films on BPO

Fatigue performance of PZT capacitors with various electrodes

(a) Pt/PZT/Pt, (b) BPO/PZT/Pt, (c) Pt/PZT/BPO
Influence of conditions on sheet resistance

Origin:
Increase of resistance at high growth temperature

• Thickness dependence
  □ $R$ v.s. $T$ □ no dependence
• Pb/Ba molar ratio
  □ XRF v.s. $T$ □ no dependence
• Grain size
  □ AFM v.s. $T$ □ no dependence
• $O_2$ vacancy
  □ Pressure dependence
    □ large dependence!
• Orientation/Crystallinity
  □ XRD □ no dependence
Gas pressure dependence

- Resistance increased with decreased gas pressure
- Resistance also increased with decreased O$_2$/Ar gas composition$^1$
  - O$_2$ defect

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Objective

• Preparation of BaPbO$_3$ thin films by rf magnetron sputtering
  ▪ Dependence on process and temperature
  ▪ Low sheet resistance
  ▪ Optimized condition
  ▪ Properties of PZT film capacitor using BaPbO$_3$

• Epitaxial growth of BaPbO$_3$
  ▪ MgO, Al$_2$O$_3$ single crystal substrates
  ▪ PZT/BPO epitaxial structure

• Deposition of Ba(Pb$_{1-x}$Bi$_x$)O$_3$ films
  ▪ Dependence on Bi substitution
  ▪ Low preparation temperature

• Preparation of BaPbO$_3$ films by laser ablation
  ▪ Dependence on process and temperature
  ▪ Optimized condition
  ▪ Preparation of PZT capacitor using BaPbO$_3$ top electrode
Preparation condition of BaPbO$_3$ thin films

**Single crystal substrates:**
- MgO(100),
- Al$_2$O$_3$(00 1),
- Al$_2$O$_3$(11 0),
- Al$_2$O$_3$(01 2)
- Pt coated MgO, Al$_2$O$_3$

**Sputtering Condition of Epitaxial BPO films**

<table>
<thead>
<tr>
<th>Preparation Equipment</th>
<th>RF Magnetron Sputter (SPF-210H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Single Crystal: MgO (001) Al$_2$O$_3$ (001), (110), (012)</td>
</tr>
<tr>
<td>Depo. Temp.</td>
<td>450 – 550 °C</td>
</tr>
<tr>
<td>RF Power</td>
<td>50 - 150 W</td>
</tr>
<tr>
<td>Depo. Pres.</td>
<td>5 - 80 mTorr</td>
</tr>
<tr>
<td>Sputtering Gas</td>
<td>Ar/O$_2$ = 50/50</td>
</tr>
<tr>
<td>Gas Flow</td>
<td>4 sccm</td>
</tr>
<tr>
<td>Target-Substrate</td>
<td>40 mm</td>
</tr>
<tr>
<td>Target</td>
<td>Pb/Ba = 1.5/1.0</td>
</tr>
</tbody>
</table>

- Dependence of orientation of films on substrate material
- Dependence on the conditions
- Fabrication PZT/BPO epitaxial structure
**Dependence on Gas pressure**

- **Low pressure**: 111 → High pressure → 001
- \( \text{Al}_2\text{O}_3 \) (110) → weak 111, \( \text{Al}_2\text{O}_3 \) (012) → 011
• At High Temperature: $\text{Al}_2\text{O}_3$ (001): 011 $\rightarrow$ 111, MgO: 111 $\rightarrow$ 001
• Highly Orientation: at 480 $^\circ$ (Al$_2$O$_3$), at 450 $^\circ$ (MgO) $\rightarrow$ Epitaxial growth
 Dependence on rf power

- BPO (111) at high rf power
XRD profiles of BaPbO$_3$ thin films on MgO(100)

- Two in-plane orientations:
  - (111) 3-fold symmetry (x 4)
  - (001) 4-fold symmetry

- Cube on cube epitaxy: BPO(100) on MgO(100)

- Sub peak for BPO (100): $\Delta \theta$ 27$\degree$

- XRD profiles of BaPbO$_3$ thin films on MgO(100)
Epitaxial BPO(111) films on Al$_2$O$_3$(00 1)

- 3-fold on 3-fold: BPO (111) on Al$_2$O$_3$(001) (the BPO was twin: 3 $\square$ 2=6)
**Epitaxial BPO films were grown on Pt layer.**

- BPO(111)/Pt/Al₂O₃(001) : 3-fold symmetry ↔ 3-fold but 2 (twin)
- BPO(111)/Pt/MgO : not BPO(001)
- BPO(111) because of Pt buffer.

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**XRD profiles of BaPbO₃ thin films on Pt/MgO(100)**

Pt/Al₂O₃(00 1)

**a)** BPO(111)[110]//Pt(111)[110]//Al₂O₃(001)[110]

**b)** BPO(111)[110]//Pt(001)[110]//MgO(001)[110]
Growth of Epitaxial $\text{BaPbO}_3$ thin films

- Epitaxial BPO films and their in-plane orientation

<table>
<thead>
<tr>
<th>BPO</th>
<th>Pt</th>
<th>Substrate</th>
<th>FWHM 1 ° on phi scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) [100]</td>
<td></td>
<td>MgO (001) [100]</td>
<td></td>
</tr>
<tr>
<td>(111) [110]</td>
<td></td>
<td>MgO (001) [110]</td>
<td>3-fold □ 4</td>
</tr>
<tr>
<td>(111) [110]</td>
<td>Pt (001) [110]</td>
<td>MgO (001) [110]</td>
<td>3-fold □ 4</td>
</tr>
<tr>
<td>(001) [110]</td>
<td></td>
<td>Al$_2$O$_3$ (001)[110]</td>
<td>4-fold □ 3</td>
</tr>
<tr>
<td>(011) [110]</td>
<td></td>
<td>Al$_2$O$_3$ (001)[110]</td>
<td>2-fold □ 3</td>
</tr>
<tr>
<td>(111) [110]</td>
<td></td>
<td>Al$_2$O$_3$ (001)[110]</td>
<td>3-fold □ 2</td>
</tr>
<tr>
<td>(111) [110]</td>
<td>Pt (111) [110]</td>
<td>Al$_2$O$_3$ (001)[110]</td>
<td>3-fold</td>
</tr>
<tr>
<td>(111) [110]</td>
<td>Pt (111) [110]</td>
<td>Al$_2$O$_3$ (001)[100]</td>
<td>3-fold □ 2</td>
</tr>
</tbody>
</table>

- Epitaxial BPO (111) films were grown on Pt(111) and Pt(100)
- Cube on cube on MgO
- Highly in-plane orientation on BPO(001)/MgO(001)
Fabrication of PZT/BPO film capacitor on Pt/Al$_2$O$_3$.

- Epitaxial PZT/BPO/Pt/Al$_2$O$_3$ structure
- PZT(111)[110]/BPO(111)[110]/Pt(111)[110]/Al$_2$O$_3$(001)[100]
- Ferroelectric DE hysteresis curve
Fabrication of PZT/BPO film capacitor on Pt/MgO

- Epitaxial PZT/BPO on Pt/MgO(100)
- PZT (111)[110]//BPO (111)[110]//Pt (001)[110]//MgO (001)[110]
Objective

• Preparation of BaPbO$_3$ thin films by rf magnetron sputtering
  □ Dependence on process and temperature
  □ Low sheet resistance
  □ Optimized condition
  □ Properties of PZT film capacitor using BaPbO$_3$

• Epitaxial growth of BaPbO$_3$
  □ MgO, Al$_2$O$_3$ single crystal substrates
  □ PZT/BPO epitaxial structure

• Deposition of Ba(Pb$_{1-x}$Bi$_x$)$_3$O$_3$ films
  □ Dependence on Bi substitution
  □ Low preparation temperature

• Preparation of BaPbO$_3$ films by laser ablation
  □ Dependence on process and temperature
  □ Optimized condition
  □ Preparation of PZT capacitor using BaPbO$_3$ top electrode
Background of Ba(Pb_{1-x}Bi_x)O_3

Subject

- Reduce preparation temperature (BPO: > 350°C)
- Low sheet resistance

Resistivities of Ba(Pb_{x}Bi_{1-x})O_3

- Dependence of crystallization temperature on Bi concentration (x)
- Dependence of Sheet resistance on x
D-E properties of PZT film capacitors annealed in vacuum

Degradation of PZT by deposition of top electrode
- BPO films were prepared at 350 °C of substrate temperature.
- PZT films may be damaged by high temperature in vacuum.

Pt top electrode was prepared at R.T.

D-E properties of Pt/PZT/Pt/TiO₂/Si capacitors

PZT films were damaged by high temperature (>350 °C) in vacuum.
- Low process temperature below 350 °C
### Experimental

<table>
<thead>
<tr>
<th>Sputtering condition of BBPO films</th>
<th>Evaluation of BBPO films</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deposition parameters</strong></td>
<td><strong>Evaluation steps</strong></td>
</tr>
<tr>
<td>Substrate SiO$_2$/Si</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Deposition Temp 250-500°C</td>
<td>→ XRF</td>
</tr>
<tr>
<td>RF Power 100W</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Deposition Press 10-100 mTorr</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Sputtering Gas Ar/O$_2$ = 50/50</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Gas Flow 4 sccm</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Target-Substrate Space 40mm</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Target Composition Ba(Bi$<em>x$Pb$</em>{1-x}$)$_{1.5}$</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Powder</td>
<td>→ XRF</td>
</tr>
<tr>
<td>Preparatory Equipment RF Magnetron Sputter (SPF 210H)</td>
<td>→ XRF</td>
</tr>
</tbody>
</table>

- Sputtering condition of BBPO films
- Evaluation of BBPO films:
  - XRF
Temperature dependence of XRD

Evaluation of crystallization temperature

BPBO films were sputtered without substrate heating

Measurement by XRD with a heater stage

Heater stage of XRD measurement for thin films (X’Pert DHS900, PANalytical)

Temperature sequence for XRD measurement ($\Delta T=10 \, ^\circ C$)
Dependence of crystallization temperature on Bi concentration

Crystallization temperature decreased with Bi substitution.
• Temperature decreased above 150 °C with Bi substitution.
• As grown films of Bi/(Bi+Pb)>50% were crystallized due to heating by rf power.

Preparation temperature may be decreased by Bi substitution
Preparation of BPBO films by sputtering with substrate heating

In case of substrate heating

Perovskite films can be obtained at 300 °C by Bi substitution (x=20%) by Bi substitution.

XRD patterns

Sheet resistance

Resistivity at low temperature (250-350 °C) can decrease by Bi substitution.

Preparation temperature may be decreased by Bi substitution.
Ferroelectric Properties of PZT film capacitors using BBPO

$D-E$ hysteresis property of $\text{Ba(Bi}_{0.2}\text{Pb}_{0.8})\text{O}_3$/PZT/ Pt/TiO$_2$/SiO$_2$/Si
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  - Low sheet resistance
  - Optimized condition
  - Properties of PZT film capacitor using BaPbO$_3$

- Epitaxial growth of BaPbO$_3$
  - MgO, Al$_2$O$_3$ single crystal substrates
  - PZT/BPO epitaxial structure

- Deposition of Ba(Pb$_{1-x}$Bi$_x$)O$_3$ films
  - Dependence on Bi substitution
  - Low preparation temperature

- Preparation of BaPbO$_3$ films by laser ablation
  - Dependence on process and temperature
  - Sheet resistance
  - Preparation of PZT capacitor using BaPbO$_3$ top electrode
Features of laser ablation deposition

- Plasma damage free
  - Top electrode (No damage to PZT layer)
  - Epitaxial growth (Low crystal defects)
- High purity films
- Composition control
  - Investigation of composition dependence
## Preparation condition of BaPbO$_3$ thin films

### Objective
- Condition dependence
- Sheet resistance
- Properties of PZT capacitor with BPO top electrodes
- Reduction of droplet formation

### Preparation conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate Temperature</td>
<td>200 – 550 ºC</td>
</tr>
<tr>
<td>Laser</td>
<td>775 nm, 200fs, 1kHz, 0.4W (PA-2001, Clark MXR Inc.)</td>
</tr>
<tr>
<td>Deposition Pressure</td>
<td>10 – 70 mTorr</td>
</tr>
<tr>
<td>Gas</td>
<td>O$_2$ 100%, 10sccm</td>
</tr>
<tr>
<td>Target</td>
<td>Ba : Pb = 1.0 : 1.8</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>0 -- 120 min</td>
</tr>
<tr>
<td>Substrate-Target Distance</td>
<td>50 mm</td>
</tr>
<tr>
<td>Substrate</td>
<td>SiO$_2$/Si (100)</td>
</tr>
</tbody>
</table>

Laser Ablation: EK-500, Eiko Co.

BPO target for laser ablation

850 ºC 2h in air
**Deposition rate**

- **Time dependence of film thickness**
  (at 350 °C, 10 mTorr)

- **Pressure dependence of film thickness**
  (at 350 °C, 60 min)

- **Deposition rate**: 2 µm/h
- **No dependence on gas pressure**
Dependence on substrate temperature

- Crystallization temperature of 350 °C
- Minimum resistance at 350 °C

Temperature dependence on resistivity

Temperature Dependence of XRD

• Crystallization temperature of 350 °C
• Minimum resistance at 350 °C
D-E properties of film capacitors with BPO electrode

D-E properties of PZT with BPO top electrodes. (BPO/PZT/ Pt/TiO$_2$/SiO$_2$/Si, 100Pa, 2h, 350°C)

Wrong D-E properties (low $Pr$, wrong curve)
- BPO films contained many clusters

Reduction of droplet formation
Improvement of surface morphology

- Reduction of droplet
  - Optimized condition (laser power, gas pressure)
  - Target (dense ceramics…)
  - Mask to eliminate large droplet

- Elimination of droplet with mask

- Influence of mask on surface morphology (1Pa, 350 kHz, 2h)
  - Large droplet decreased with mask.
  - Deposition rate also decreased.
  - Optimization of mask size, position, gas pressure
Conclusion

• BPO film deposition on SiO$_2$/Si substrates
  ▪ Perovskite BPO films were obtained at 350 $\degree$ $\sim$ 550 $\degree$ (with Subst. heat).
  ▪ Sheet resistance decreased with decreasing temperature.
    → Low temperature deposition
  ▪ D-E hysteresis was observed for PZT capacitors used BPO electrodes, however fatigue property was slightly improved.
    Subject: Optimization of deposition condition of PZT on BPO

• BPO film deposition on single crystal substrates
  ▪ BPO films were epitaxially grown on MgO(100) and Al$_2$O$_3$(00 $\cdot$1) substrates.
  ▪ Orientation and in-plane orientation of the BPO were widely varied by the sputtering condition.
  ▪ Epitaxial PZT films were also grown on the BPO.
    → Epitaxial capacitor structure
• Ba(Pb$_x$Bi$_{1-x}$)O$_3$ (BPBO) film deposition
  - Low crystallization temperature by Bi substitution (400 $^\circ$C $\rightarrow$ 350 $^\circ$C at $x=20\%)$
  - BPBO ($x=20\%)$ was obtained at 300 $^\circ$C of substrate temperature.
  - Sheet resistance at low substrate temperature decreased with Bi substitution.
    $\rightarrow$ Low temperature deposition

• BPO film deposition by laser ablation
  - Similar preparation condition dependence (perovskite BPO and the minimum resistance were obtained at 350 $^\circ$C)
  - $D$-$E$ property of PZT capacitors with BPO top electrode was measured, and $Pr$ was low.
  - Many droplet and wrong surface morphology

Subject: Improvement by eliminator (mask) and preparation condition.