PREPARATION OF $BaPbO_3$ ELECTRODE THIN FILMS BY RF MAGNETRON SPUTTERING AND THEIR PROPERTIES

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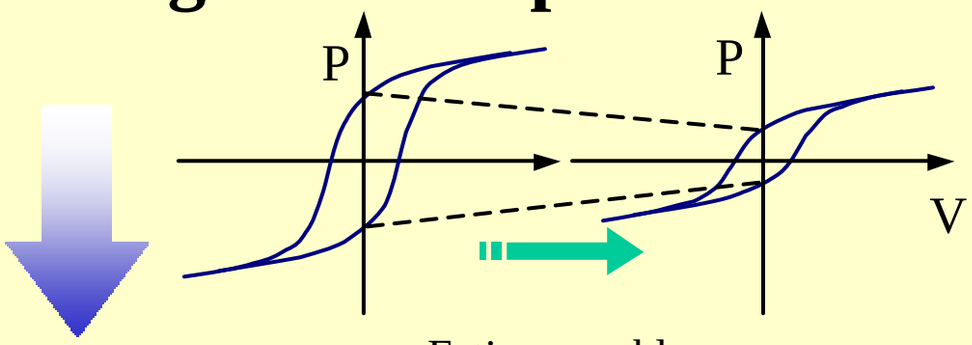
Background *-Electrode materials for FeRAM & $BaPbO_3$-*

Electrode for FeRAM

Degradation of FeRAM capacitors

fatigue and imprint



Fatigue problem

Electrode materials for the capacitors

- **Ir** : reduce Pb diffusion
- **IrO_2, RuO_2 :** oxide
- **$SrRuO_3$:** perovskite

similar in crystal structure and composition to PZT

Barium metaplumbate

$BaPbO_3$ (BPO)

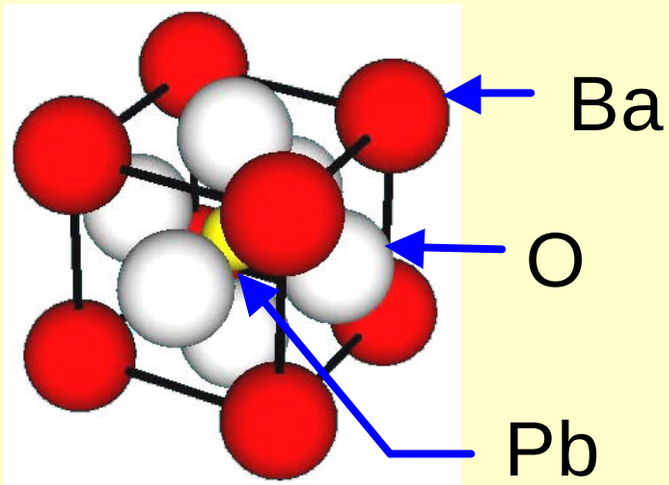
Feature of $BaPbO_3$

1. Conductive Oxide

resistivity (Ωcm)

$SrRuO_3$	Perovskite a = 5.56, b = 5.55, c = 7.89	1×10^{-3}
IrO_2	rutile : a = 4.50, c = 3.15	4.9×10^{-5}
$(La,Sr)CoO_3$	perovskite : a = 3.81	$< 10^{-4}$
$BaPbO_3$	**perovskite : a = 4.265**	**3×10^{-4}**

2. Perovskite structure



Unit cell for BPO(perovskite)
Cubic、a = 4.265 Å、α = β = γ = 90 °

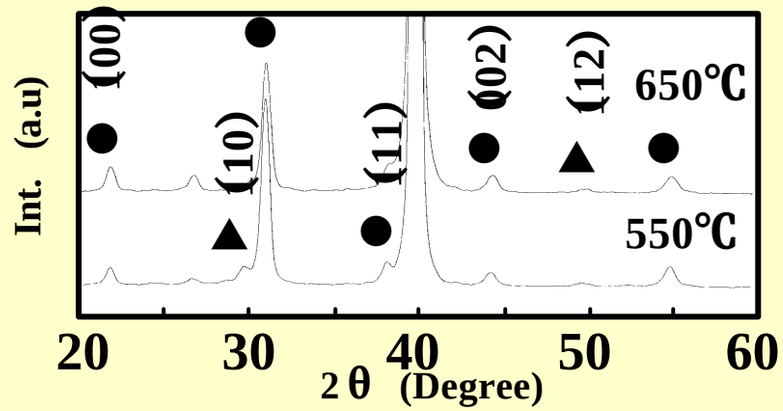
3. Pb included

→ 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℃ sintering
  - + ρ : 1.6×10^{-2} Ωcm (SiO_2/Si)
    (Bulk: 3×10^{-4} Ωcm *)
- ***Recently***, fatigue free PZT film capacitors used BPO electrode. (on SiO_2/Si)*3



XRD profile of PZT/BPO by CSD

*1 T. Azuma, J. Ceram. Soc. Japan, 103 (1995) 822
*2 I. Kawakami et al. IFFF 2003
*3 Yih-Rong, Luo et. al., Appl. Phys. Lett., **79**, 3669 (2001)

Preparation of high quality BPO thin films

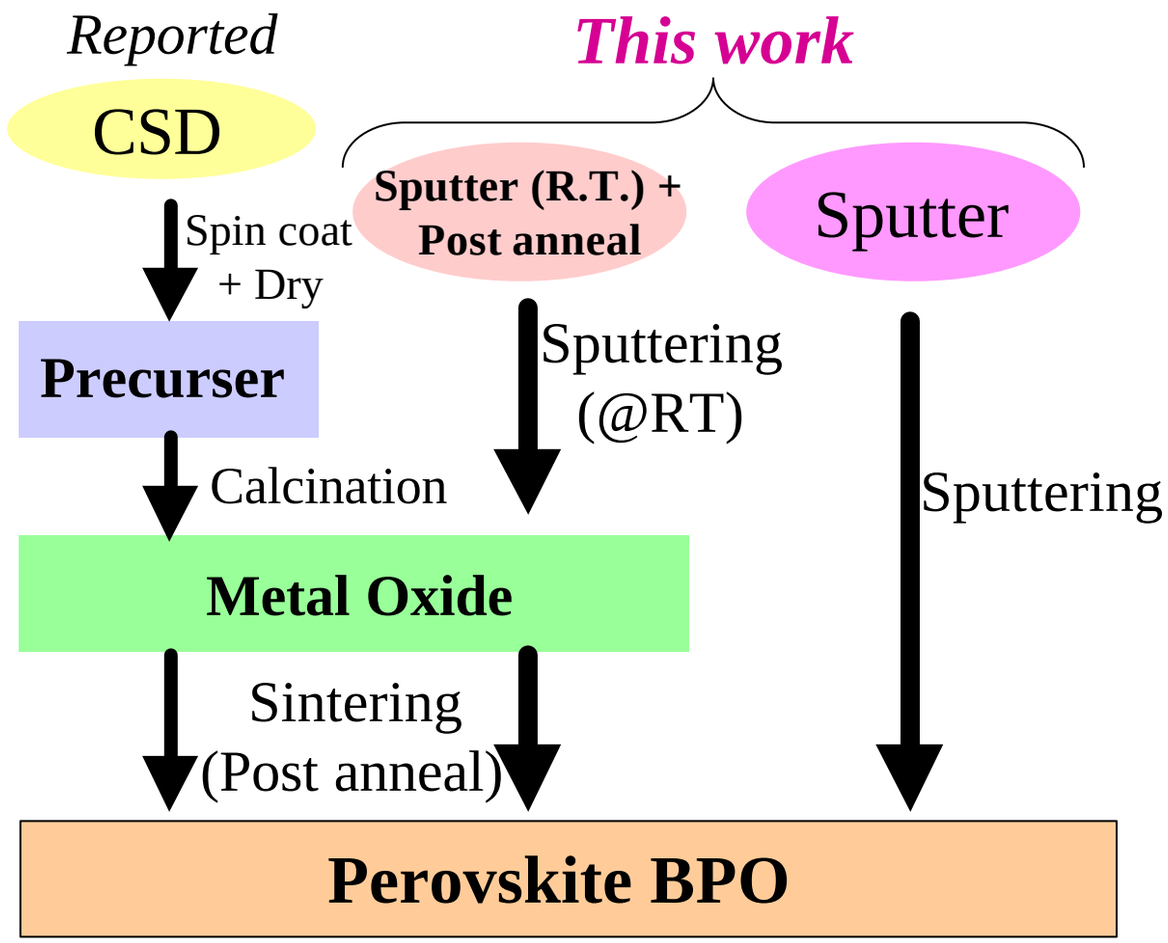
- Preparation of $BaPbO_3$ thin films by rf magnetron sputtering
  - ⇒ Dependence on process and temperature
- Epitaxial growth of $BaPbO_3$
  - ⇒ Al2O3, MgO substrates
- Deposition of $Ba(Pb_{1-x}Bi_x)O_3$ films
  - ⇒ Low sheet resistance & preparation temperature
- Preparation of $BaPbO_3$ films by laser ablation

PREPARATION OF $BaPbO_3$ ELECTRODE THIN FILMS BY RF MAGNETRON SPUTTERING AND THEIR PROPERTIES

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_2O_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



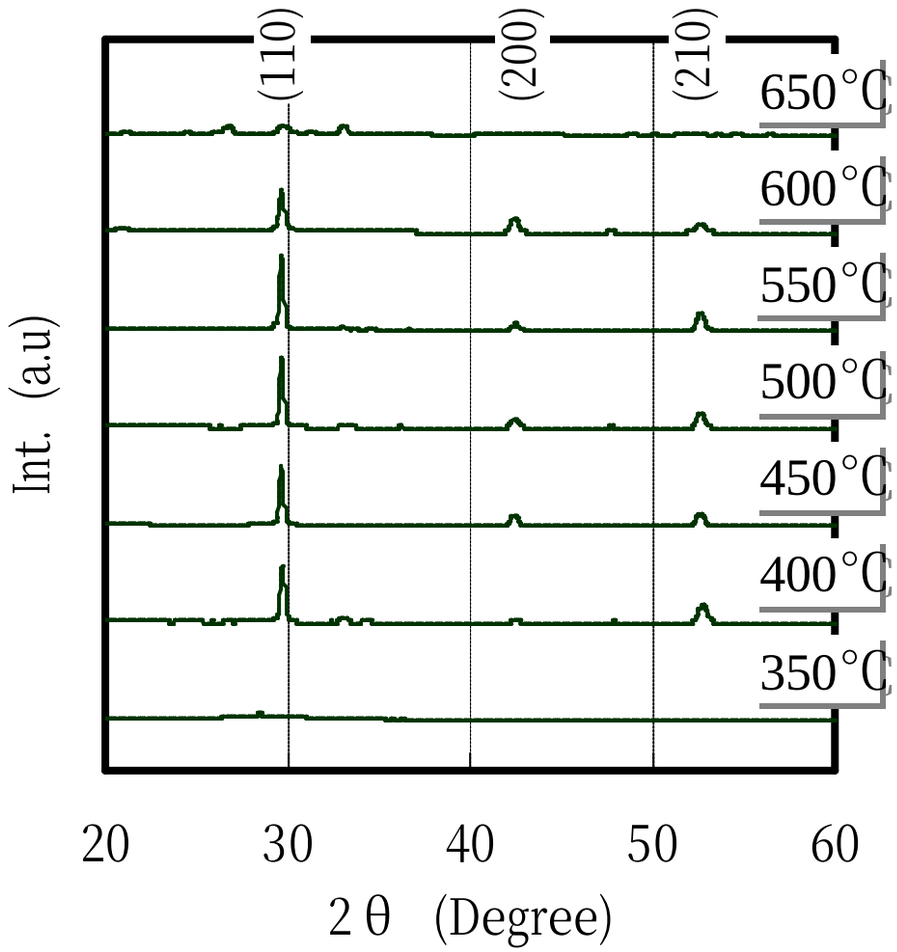
- **Dependence of crystallinity of BPO films on the preparation methods.**
- **Dependence of the films on post anneal & substrate temperatures.**

Preparation conditions

	Post anneal	Substrate heating
Substrate Temperature	R.T.	100 – 550 ℃
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 ℃ 30 min, in Air	–

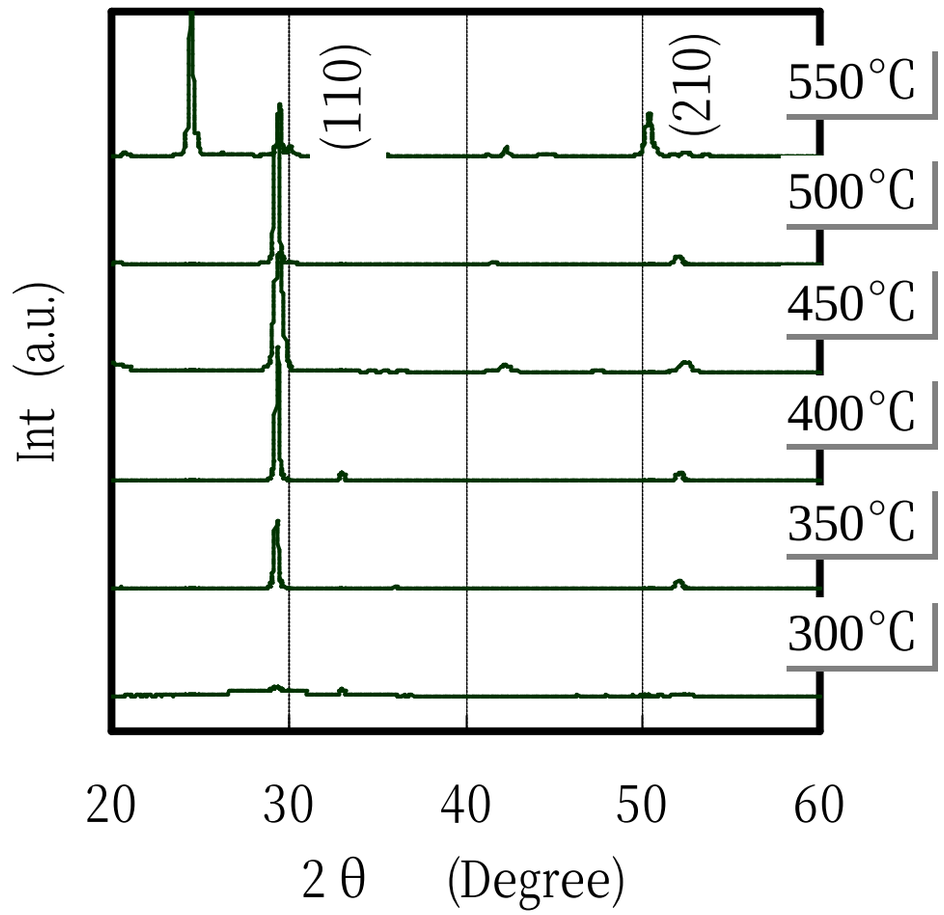
equipment :rf magnetron sputter, SPF-210H (Anelva)

XRD profiles of $BaPbO_3$ thin films



Post annealing

→ 400°C – 650°C

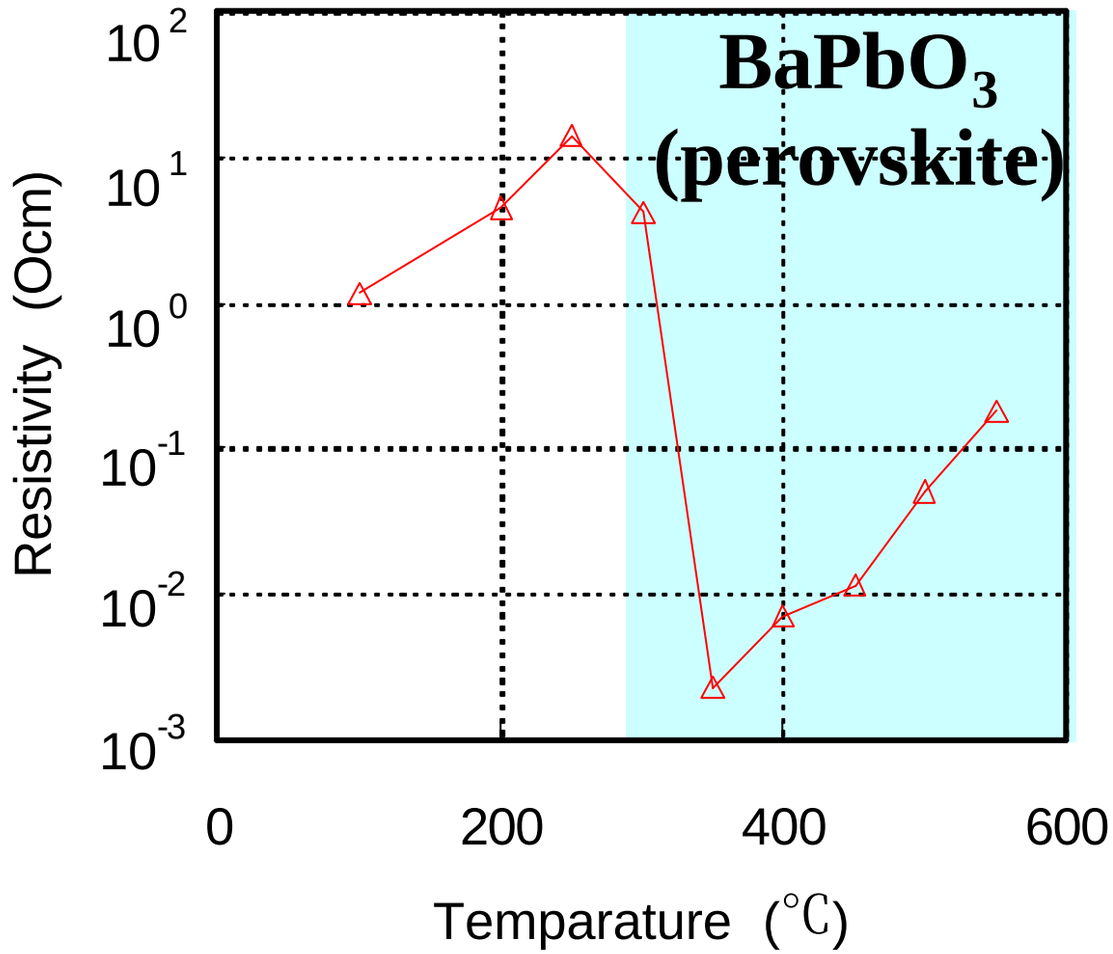


Substrate heating

→ 350°C – 550°C

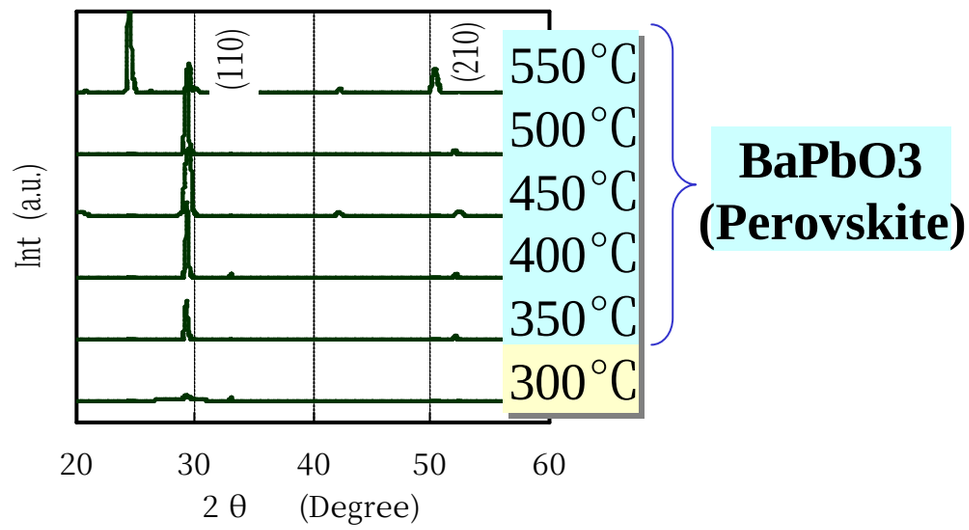
BPO thin films were prepared at low temperature
550°C(CSD) → 350 °C (Sputtering)

Sheet resistance of $BaPbO_3$ thin films



Resistivity : four probe method

- Probe head (K504RB, Kyowariken)
- Space between terminals: 1 mm
- Terminals R: 150 μ m
- Materials: WC

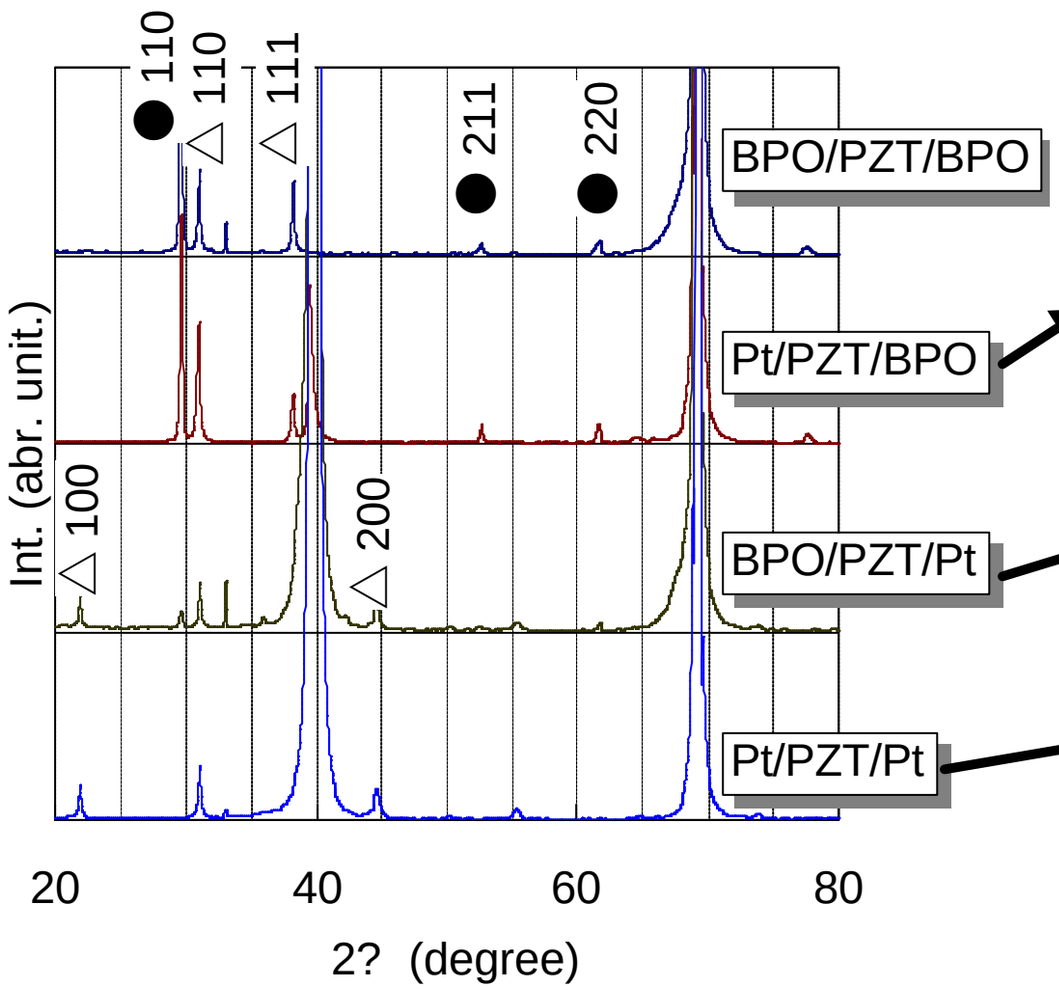


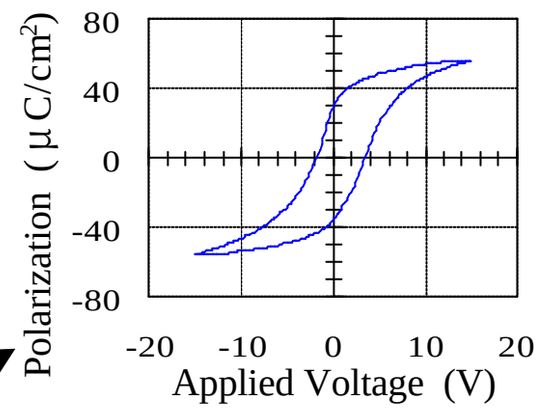
Resistivity of BPO thin films prepared at various temperatures

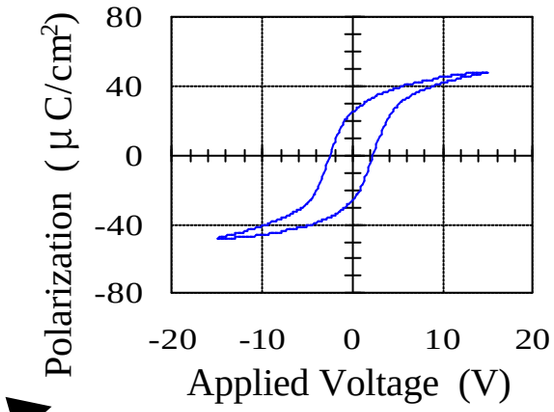
Perovskite $BaPbO_3$ thin films have low resistivity

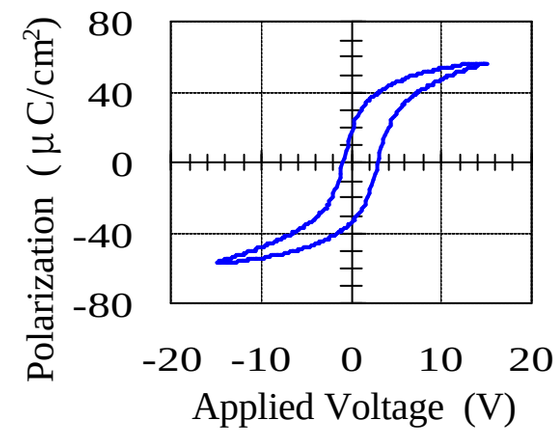
$2.5 \times 10^{-3} \sim 2 \times 10^{-1}$ Ωcm

Fabrication of PZT/BPO capacitor





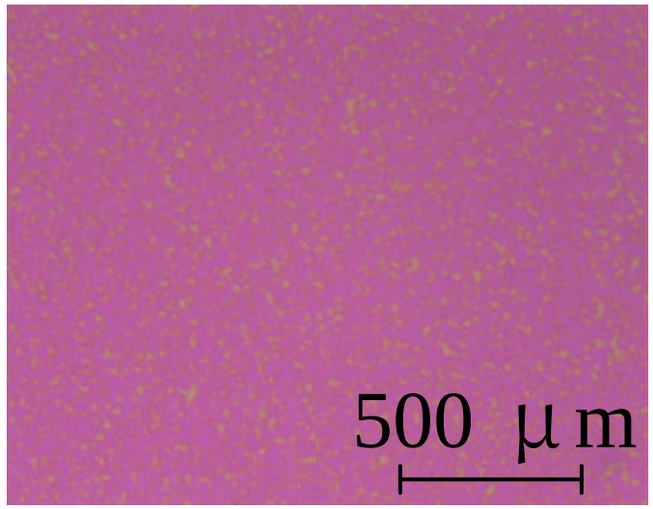




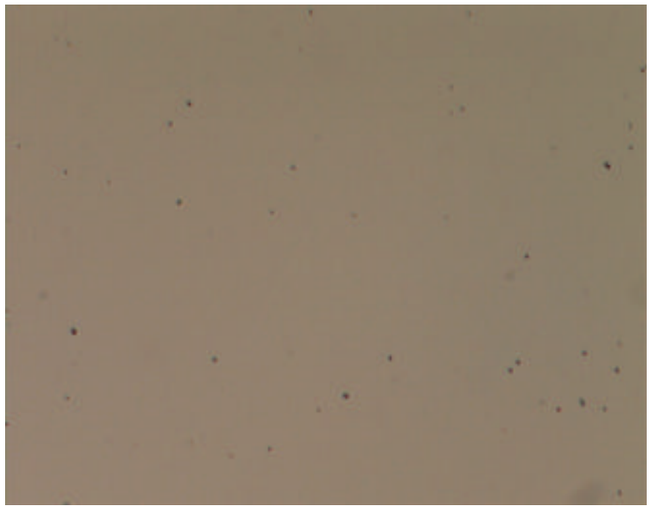
● BPO、△ PZT

	2*P*r (μC/cm^2)	2*E*c (kV/cm)
Pt/PZT/Pt	**53.1**	166
BPO/PZT/Pt	**55.7**	215
Pt/PZT/BPO	**74.7**	233

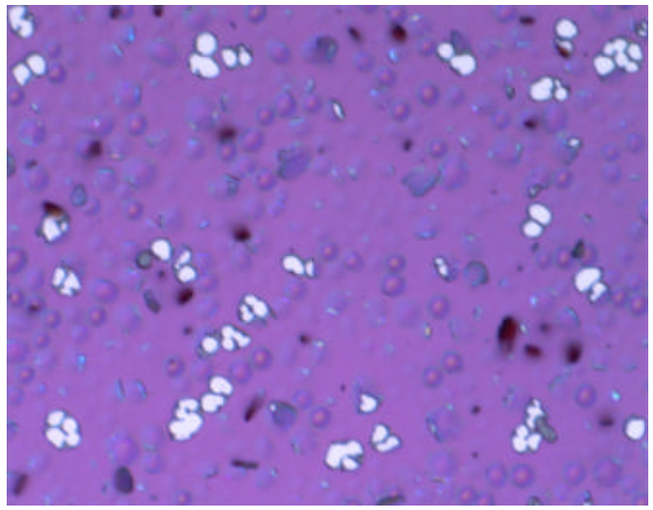
Adhesion of $BaPbO_3$ films



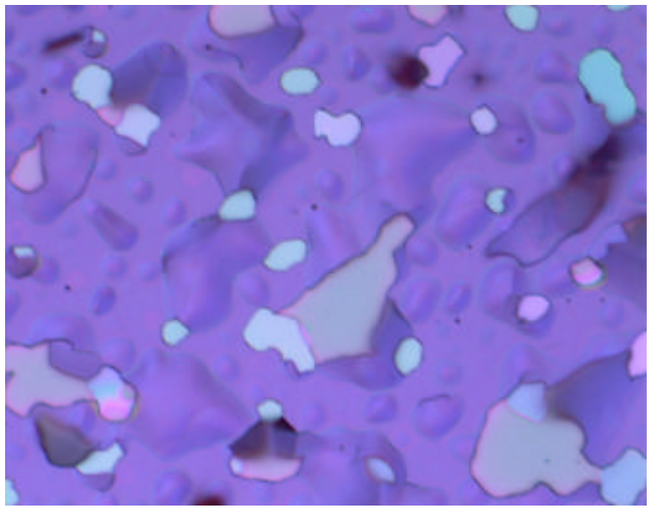
PZT/Pt//Si



BPO//Si



PZT/BPO/Pt//Si



PZT/BPO//Si

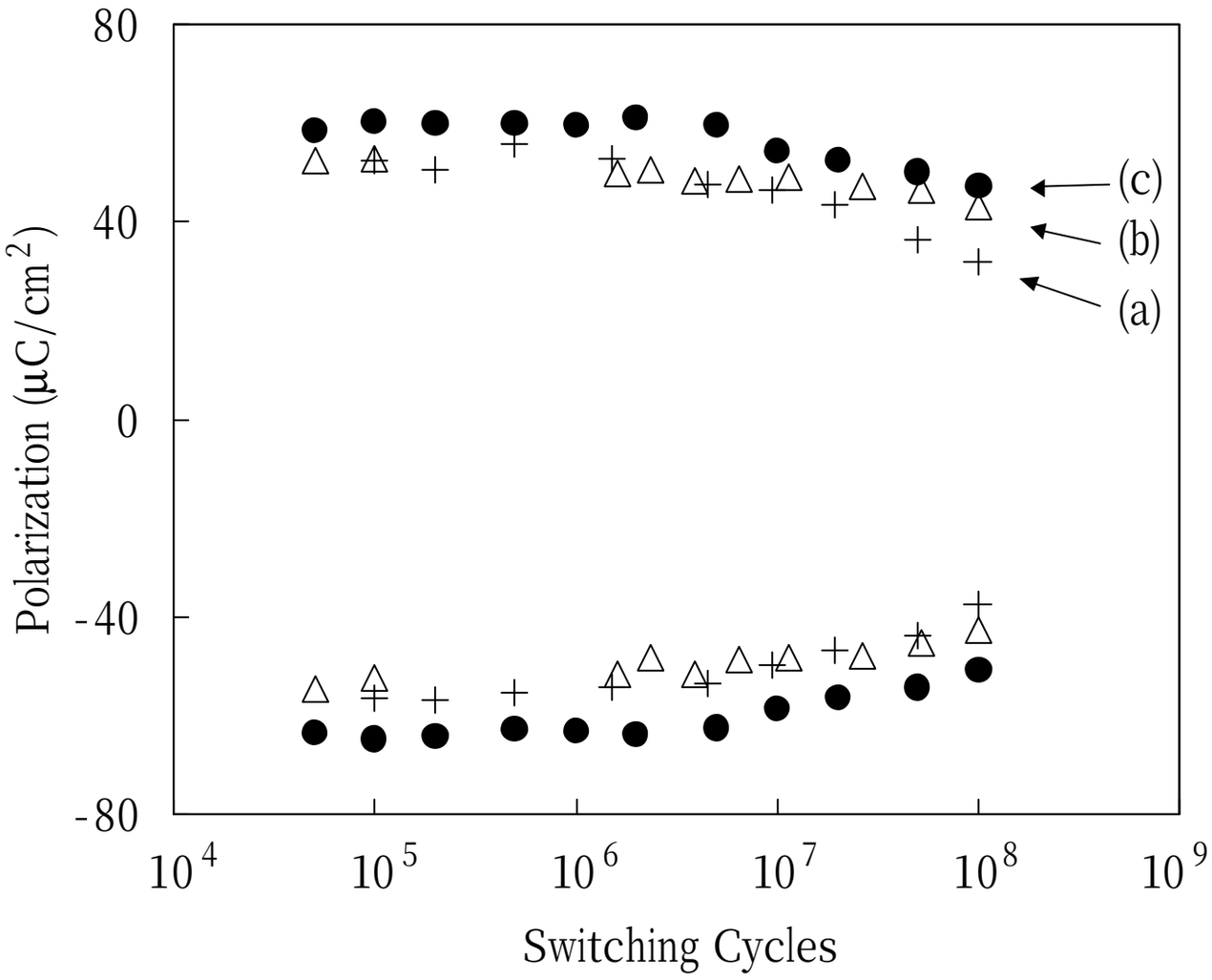
Films surface after annealing

Annealing after deposition PZT films (600℃,30 min)

Peeling off BPO films from substrates

Improvement of the adhesion

Fatigue performance



(a) Pt/PZT/Pt, (b) BPO/PZT/Pt, (c) Pt/PZT/BPO

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 differ that of Pt

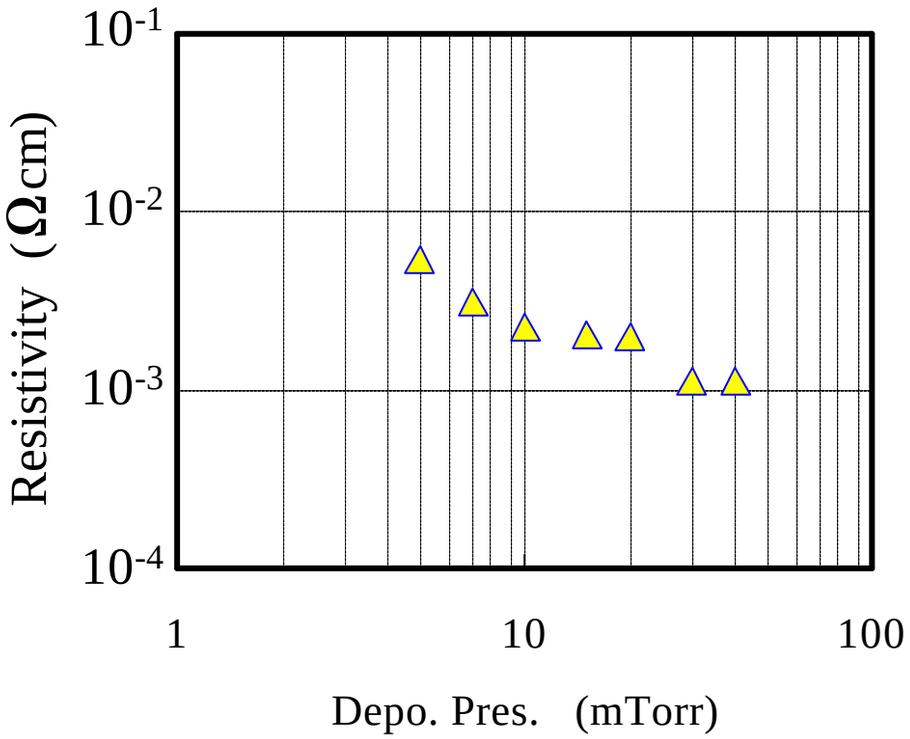
Improvement for crystallinity of PZT thin films on BPO

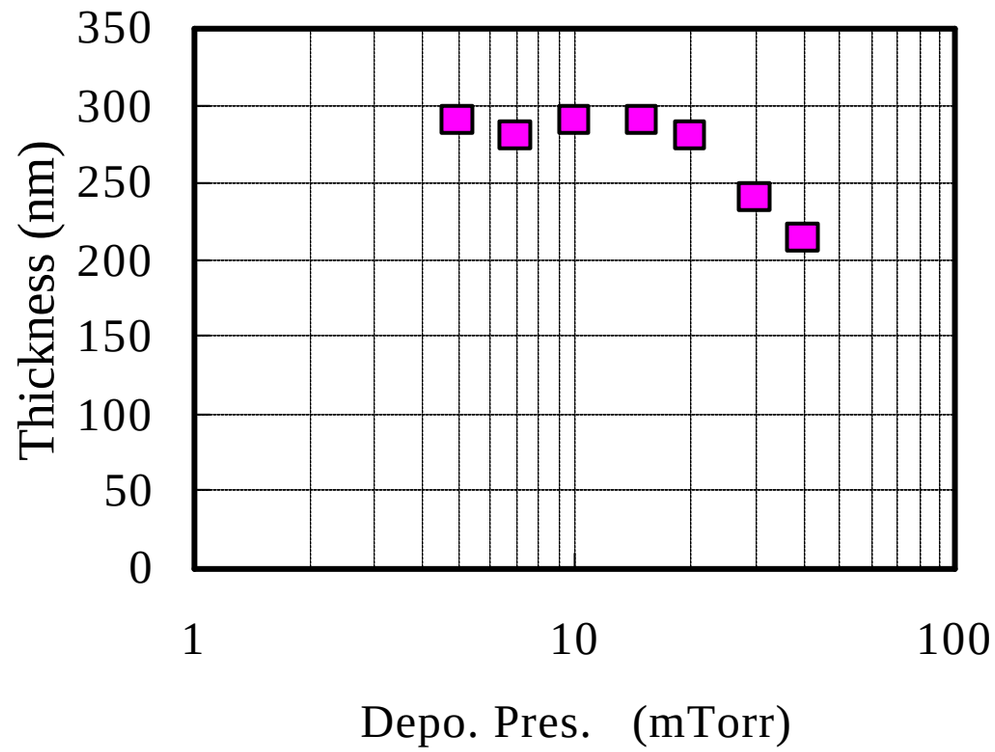
Influence of conditions on sheet resistance

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

*1: M. Suzuki, Jpn. J. Appl. Phys. 32 (1993) 2640

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  - ⇒ Properties of PZT film capacitor using $BaPbO_3$
- Epitaxial growth of $BaPbO_3$
  - ⇒ MgO, Al_2O_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_2O_3(00·1),

Al_2O_3(11·0),

Al_2O_3(01·2)

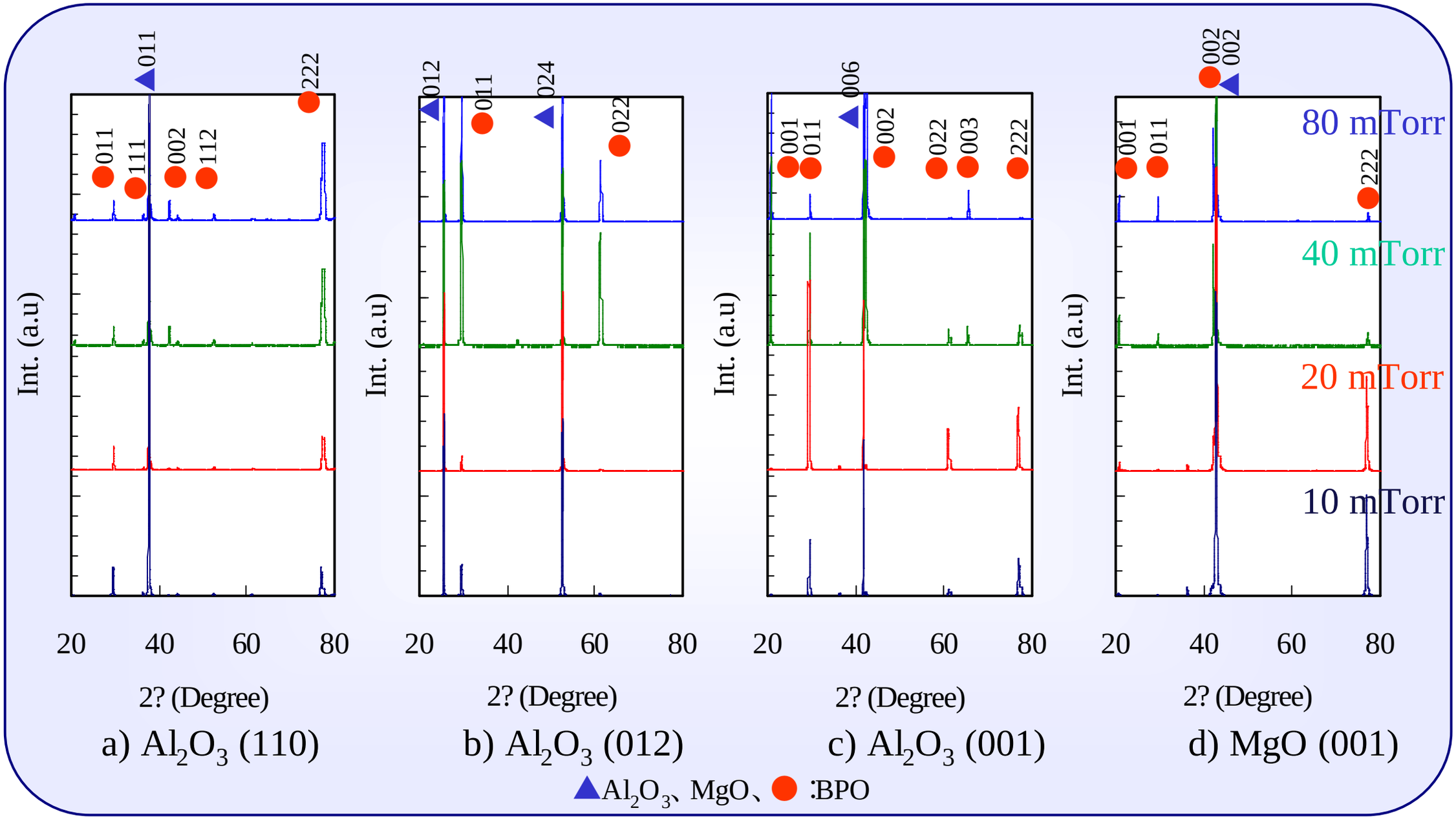
Pt coated MgO, Al_2O_3

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

Sputtering Condition of Epitaxial BPO films

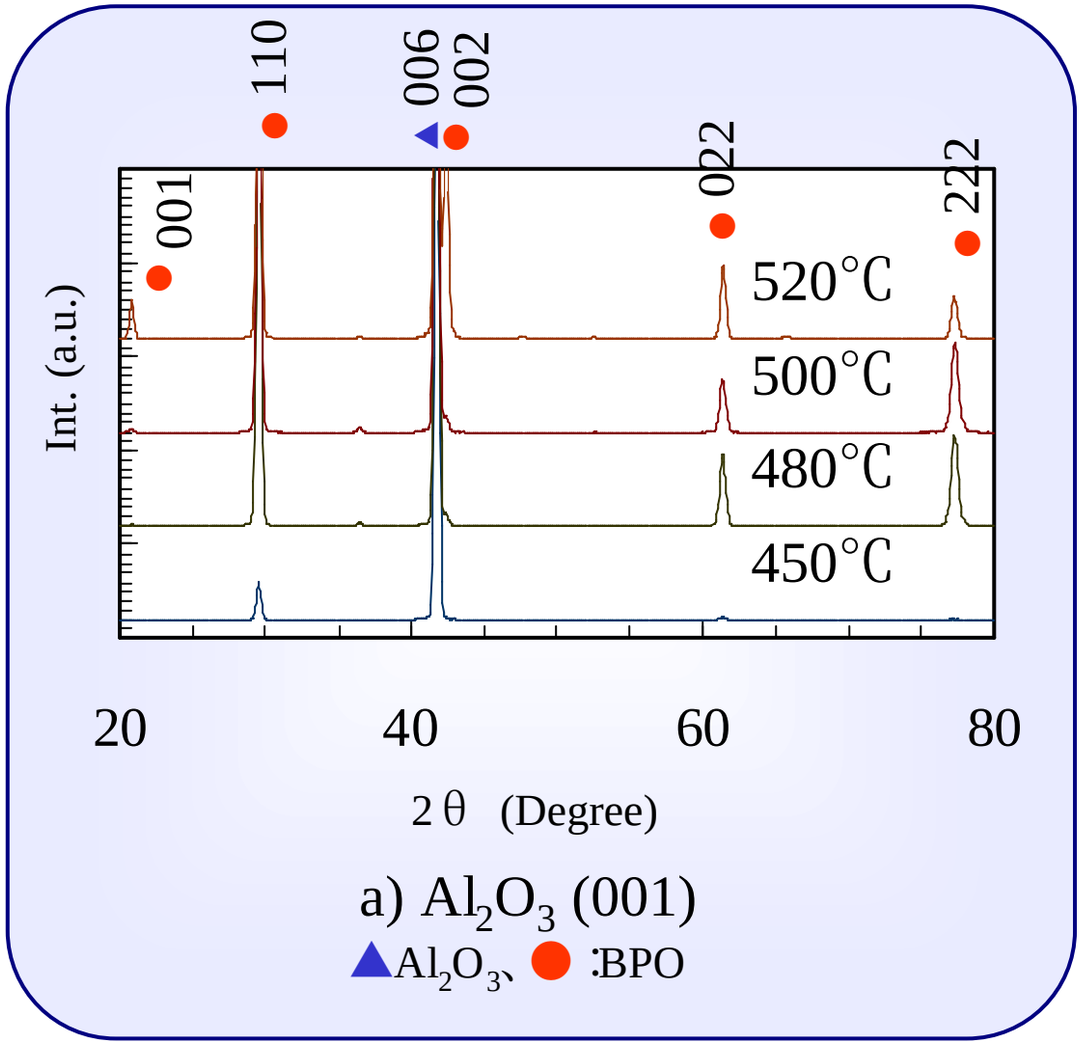
Preparation Equipment	RF Magnetron Sputter (SPF-210H)
Substrate	Single Crystal: MgO (001) Al_2O_3 (001), (110), (012)
Depo. Temp.	450 – 550℃
RF Power	50 - 150 W
Depo. Pres.	5 - 80 mTorr
Sputtering Gas	Ar/O_2 = 50/50
Gas Flow	4 sccm
Target-Substrate	40 mm
Target	Pb/Ba = 1.5/1.0

Dependence on Gas pressure



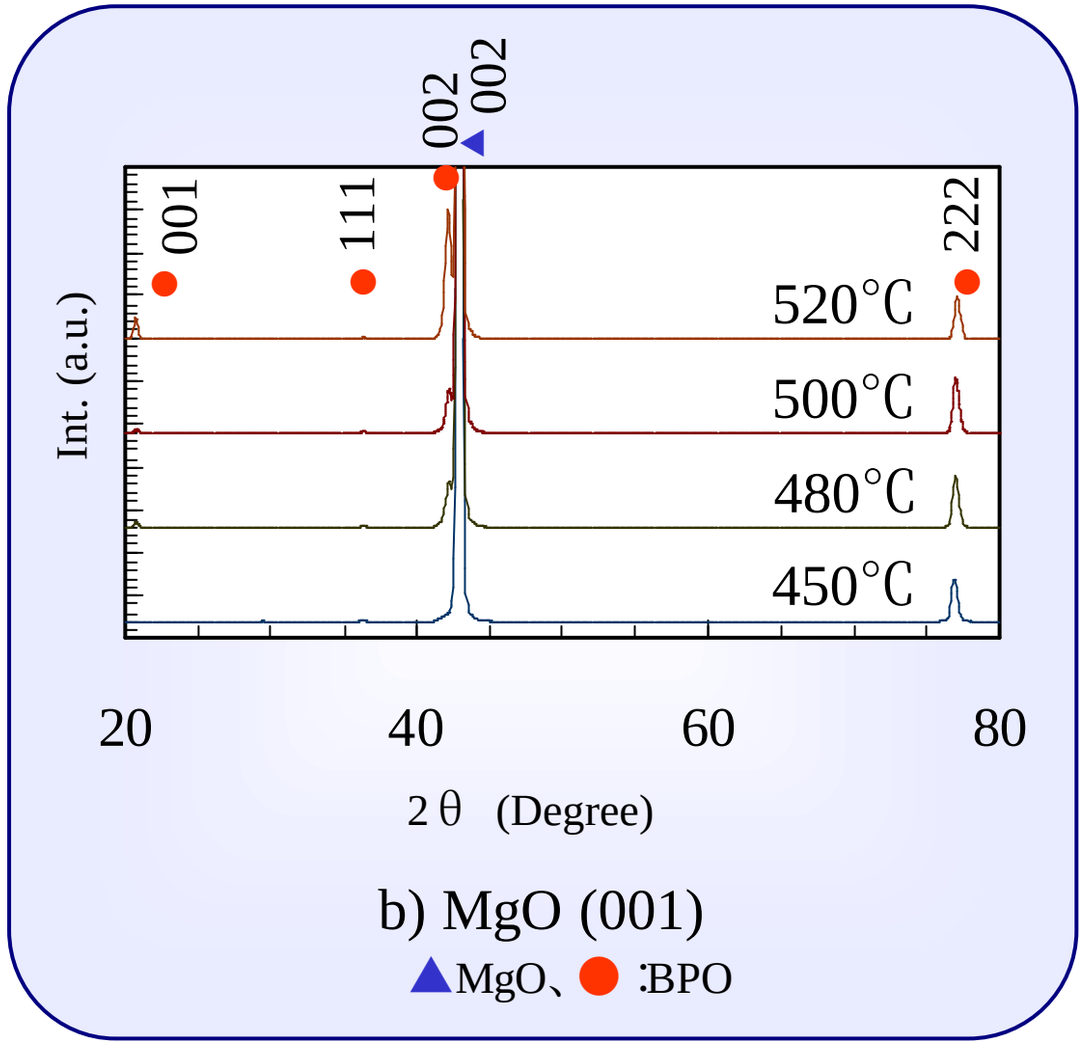
- Low pressure→ 111 、High pressure→ 001
- Al_2O_3 (110)→weak 111 、 Al_2O_3 (012) → 011

Dependence on substrate temperature



a) Al_2O_3 (001)

▲Al_2O_3、● :BPO

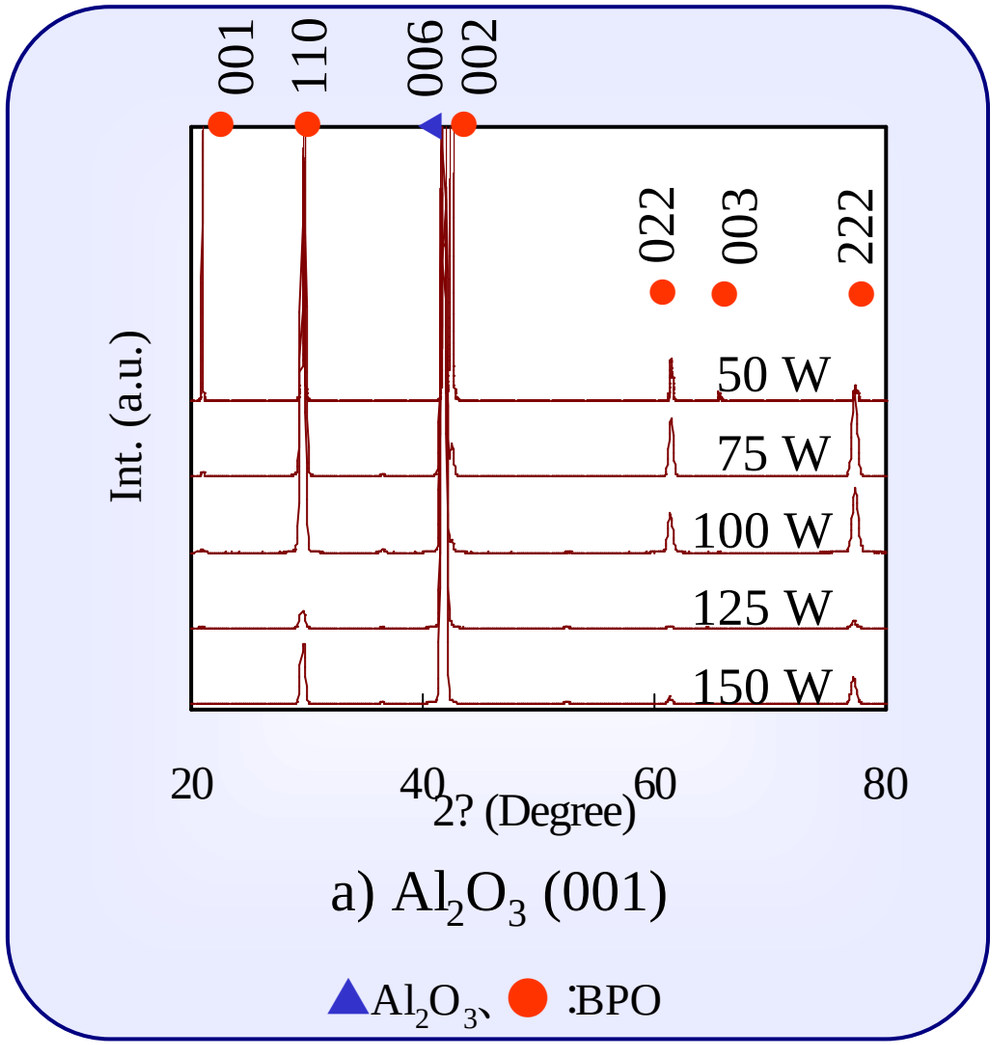


b) MgO (001)

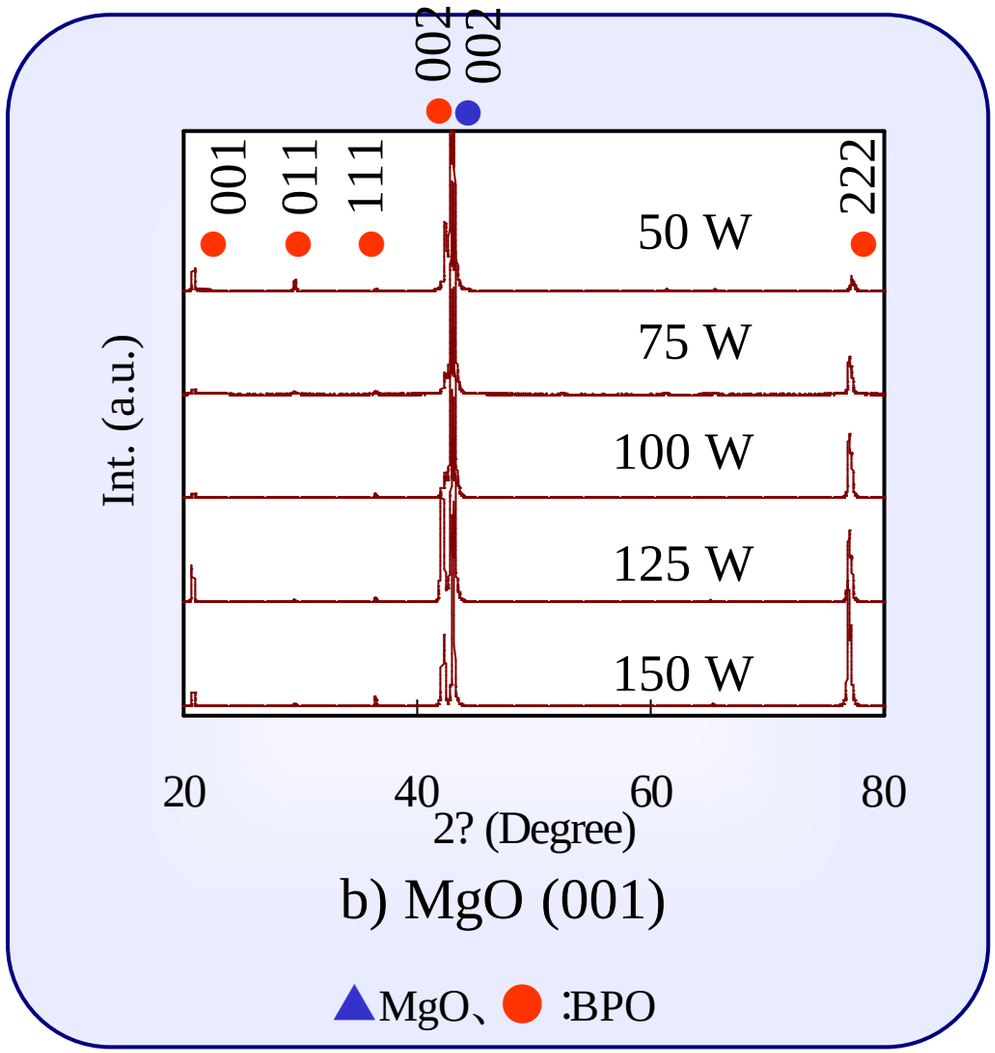
▲MgO、● :BPO

- At High Temperature: Al_2O_3 (001): 011 → 111、MgO: 111 → 001
- Highly Orientation: at 480℃ (Al_2O_3), at 450℃ (MgO)
  → Epitaxial growth

Dependence on rf power



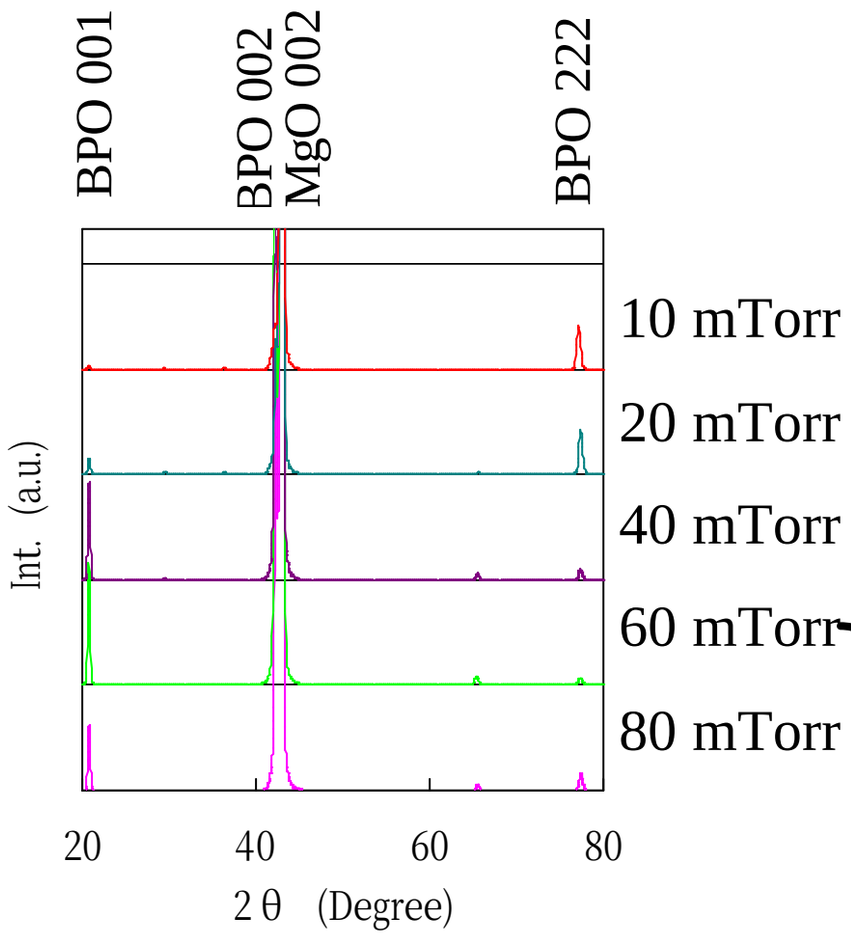
a) Al_2O_3 (001)

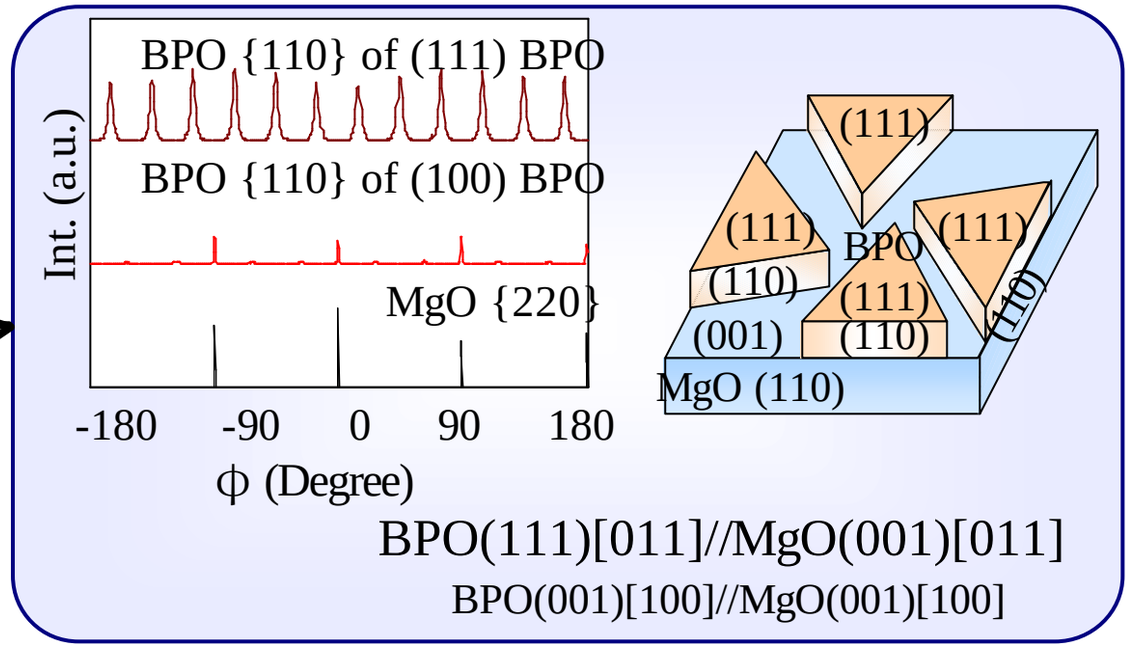


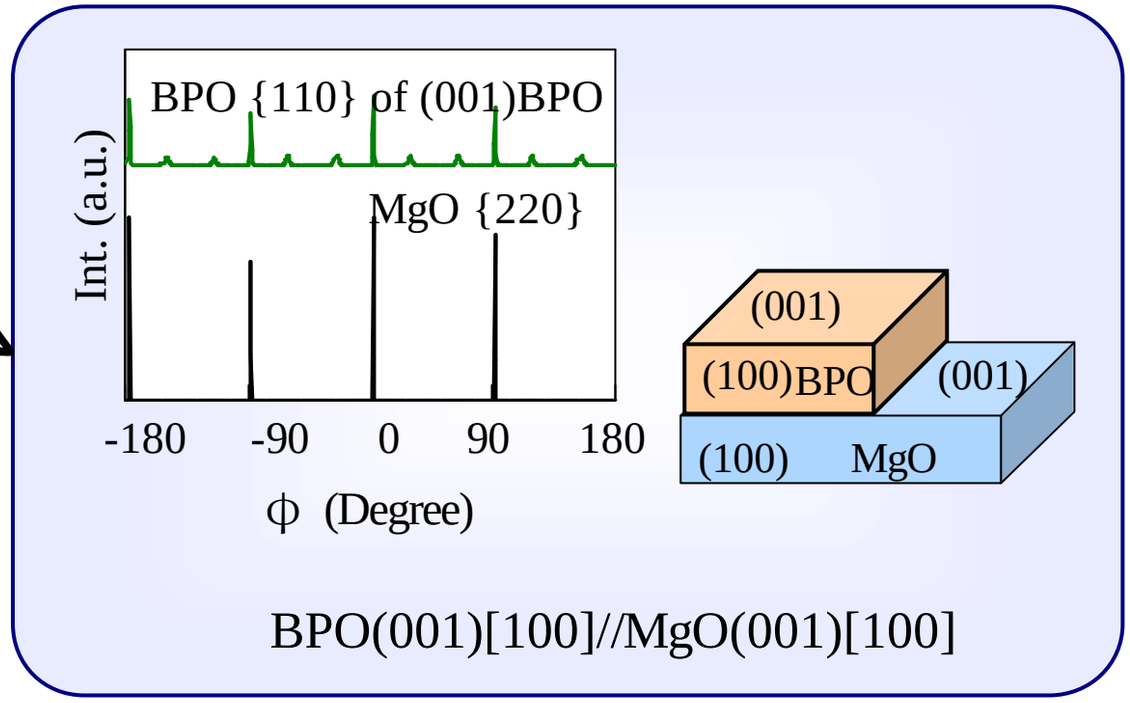
b) MgO (001)

- BPO (111) at high rf power

XRD profiles of $BaPbO_3$ thin films on MgO(100)



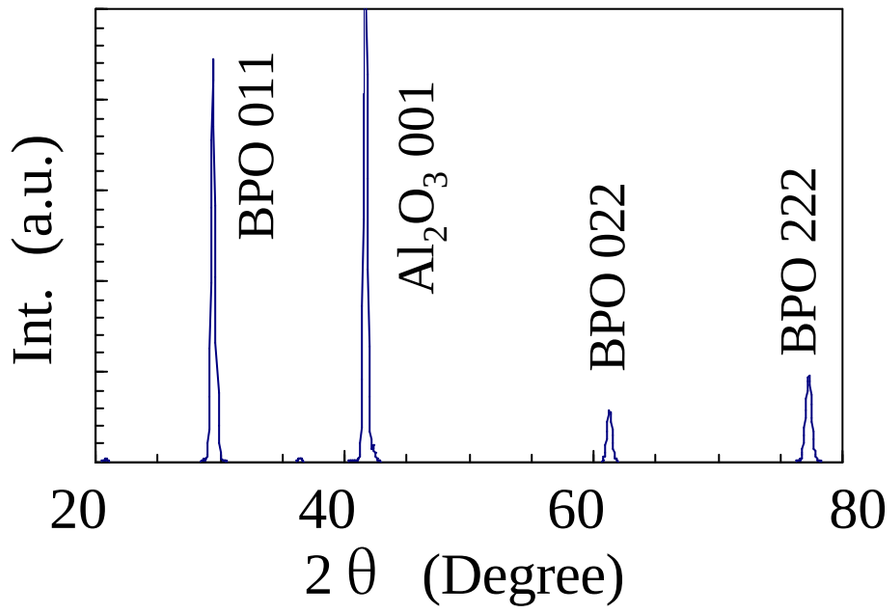


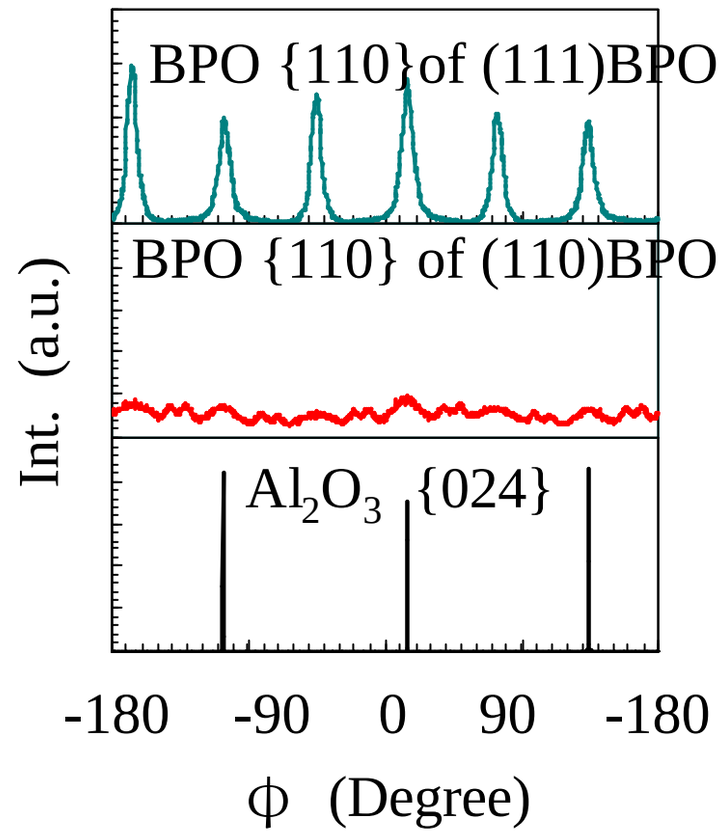


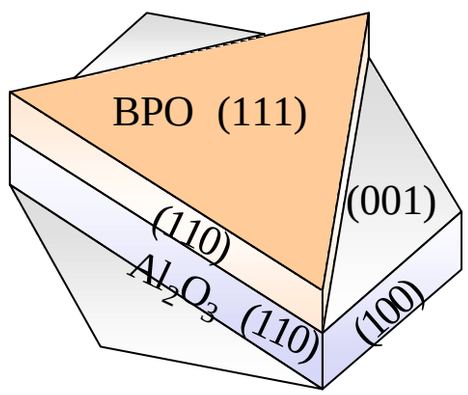
- **Two in-plane orientation**:
  (111) 3-fold symmetry (x 4) or
  (001) 4-fold symmetry
- **Cube on cube epitaxy**:
  BPO(100) on MgO(100)
- Sub peak for BPO (100) : ±27. 5

XRD profiles of $BaPbO_3$ thin films

on Al_2O_3(00 •1)





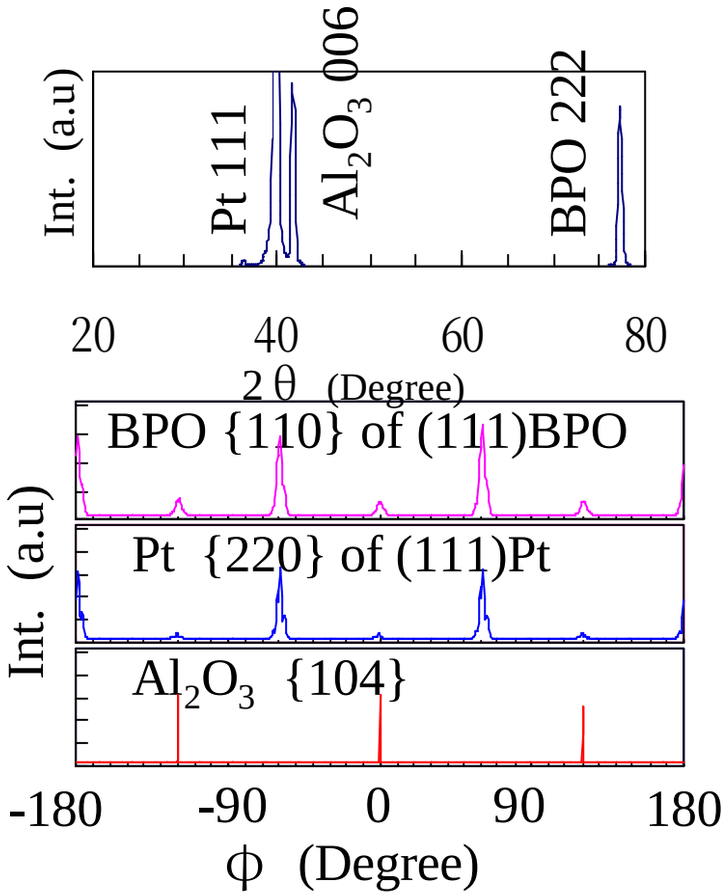


BPO(111)[110]//Al_2O_3(001)[110]

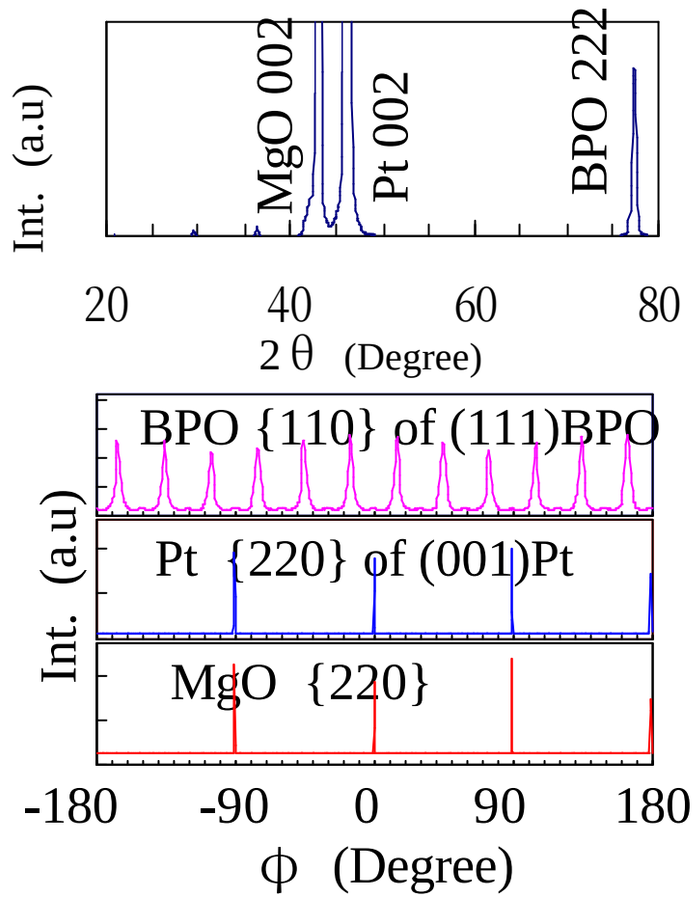
- **Epitaxial BPO(111) films** on Al_2O_3(001)
- 3-fold on 3-fold: BPO (111) on Al_2O_3(001)

(the BPO was twin: 3×2=6)

XRD profiles of $BaPbO_3$ thin films on Pt/MgO(100) Pt/Al_2O_3(00 •1)



a) BPO(111)[110]//Pt(111)[110]//Al_2O_3(001)[110]



b) BPO(111)[110]//Pt(001)[110]//MgO(001)[110]

Epitaxial BPO films were grown on Pt layer.

- BPO(111)/Pt/Al_2O_3(001) ：3-fold symmetry ← 3-fold ×2 (twin)
- BPO(111)/Pt/MgO ：not BPO(001)

→ BPO (111) because of Pt buffer.

Growth of Epitaxial $BaPbO_3$ thin films

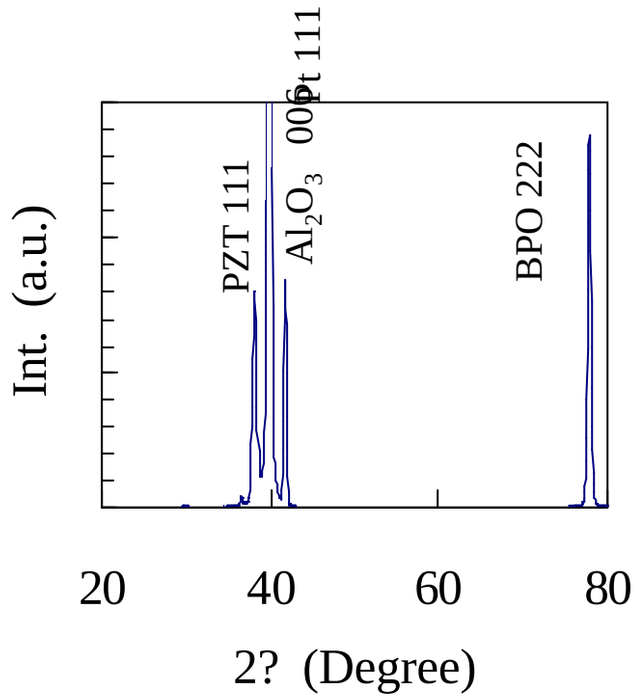
- **Epitaxial BPO films and their in-plane orientation**

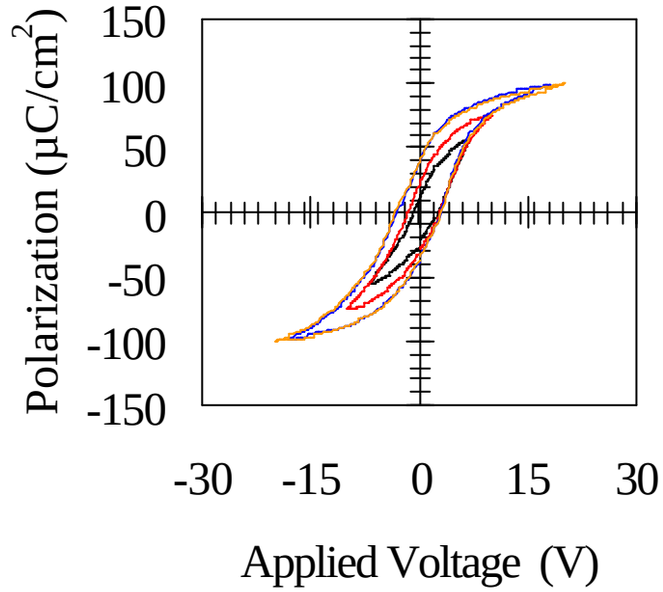
BPO	Pt	Substrate	
(001) [100]	none	MgO (001) [100]	FWHM 1 ° on phi scan 0±27.3 ° at rf 50W
(111) [110]	none	MgO (001) [110]	3-fold ×4
(111) [110]	Pt (001) [110]	MgO (001) [110]	3-fold ×4
(001) [110]	none	Al_2O_3 (001)[110]	4-fold ×3
(011) [110]	none	Al_2O_3 (001)[110]	2-fold ×3
(111) [110]	none	Al_2O_3 (001)[110]	3-fold ×2
(111) [110]	Pt (111) [110]	Al_2O_3 (001)[110]	3-fold
(111) [110]	Pt (111) [110]	Al_2O_3 (001)[100]	3-fold ×2

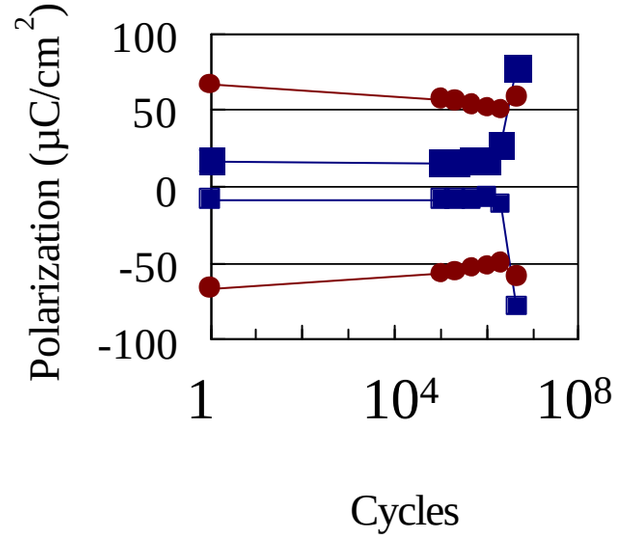
- Epitaial BPO (111) films were grown on Pt(111) and Pt(100)
- Cube on cube on MgO
- Highly in-plane orientation on BPO(001)/MgO(001)

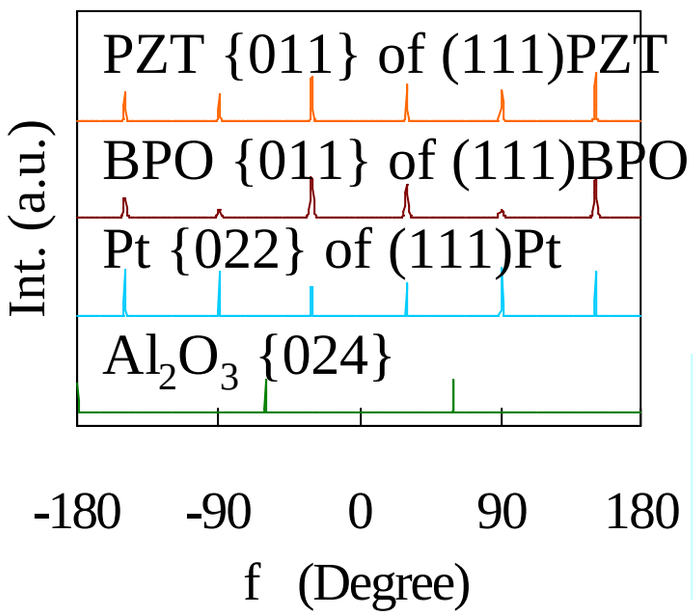
Fabrication of PZT/BPO film capacitor

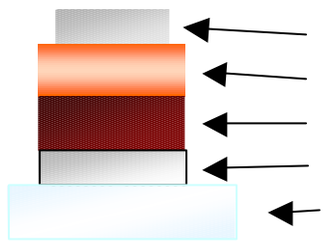
on Pt/Al_2O_3











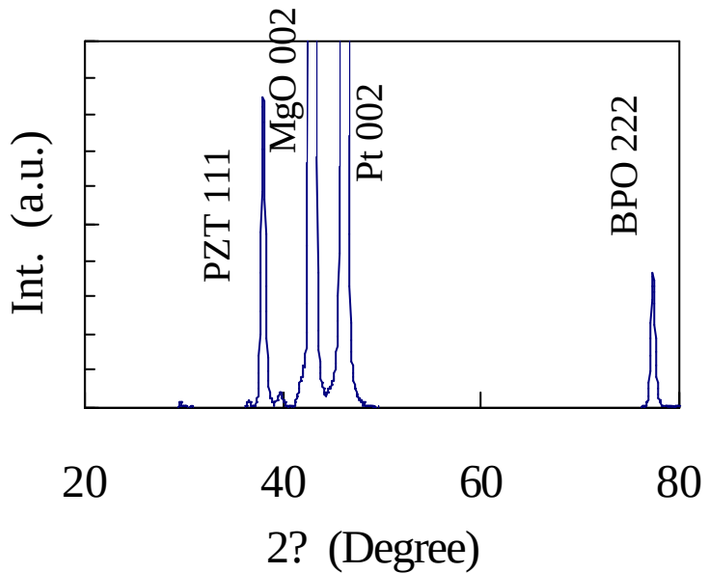
Pt top electrode: 125 nm、ϕ0.1 mm
PZT ferroelectric layer: 360 nm
BPO Bottom electrode: 450 nm
Pt buffer layer: 60 nm
Al_2O_3 substrate

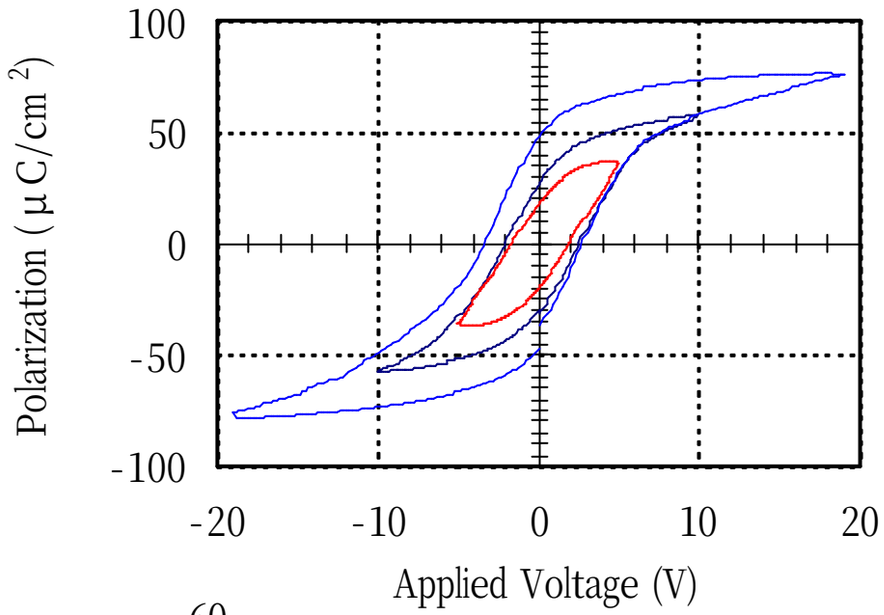
- Epitaxial PZT/BPO/Pt/Al_2O_3 structure

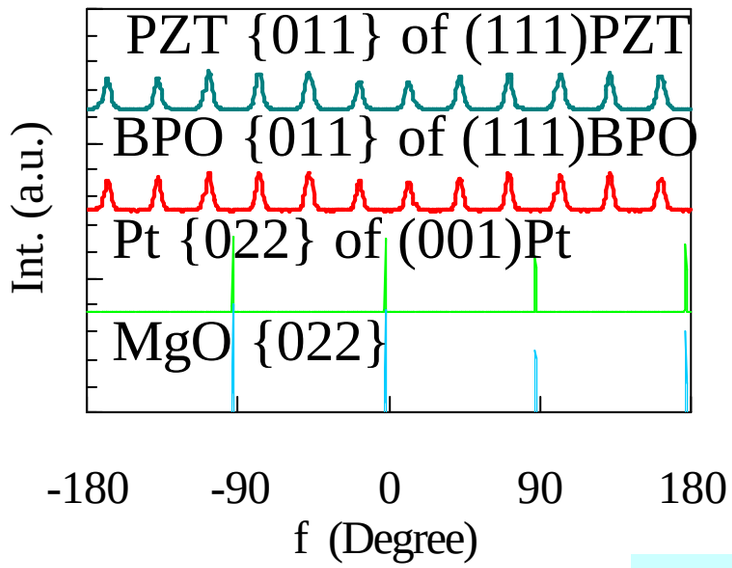
PZT(111)[110]//BPO(111)[110]//Pt(111)[110]//Al_2O_3(001)[100]

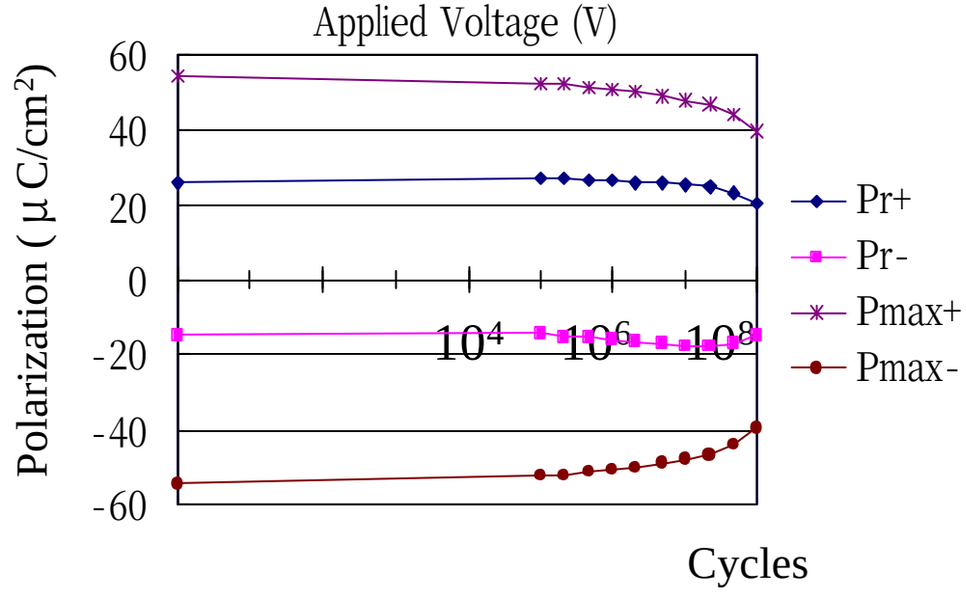
- Ferroelectric *DE* hysteresis curve

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]

PREPARATION OF $BaPbO_3$ ELECTRODE THIN FILMS BY RF MAGNETRON SPUTTERING AND THEIR PROPERTIES

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_2O_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

Background of $Ba(Pb_{1-x}Bi_x)O_3$

Subject

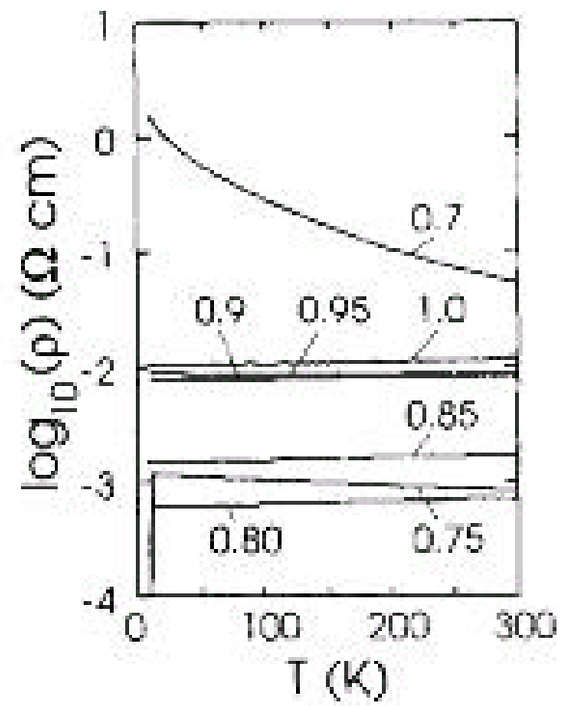
- Reduce preparation temperature
  (BPO：＞350℃)
- Low sheet resistance
  → Bi substitution

$Ba(Pb_{1-x}Bi_x)O_3$ (BPBO)

Properties of BPBO ceramics as super conductor were widely investigated.

M.Suzuki, JJAP 32(1993)2640
D.T.Marx, PHYSICAL REVIEW B 46(1992)1144
S.Tajima, PHYSICAL REVIEW B 35(1987)696

→ Resistivity decrease with Bi substitution



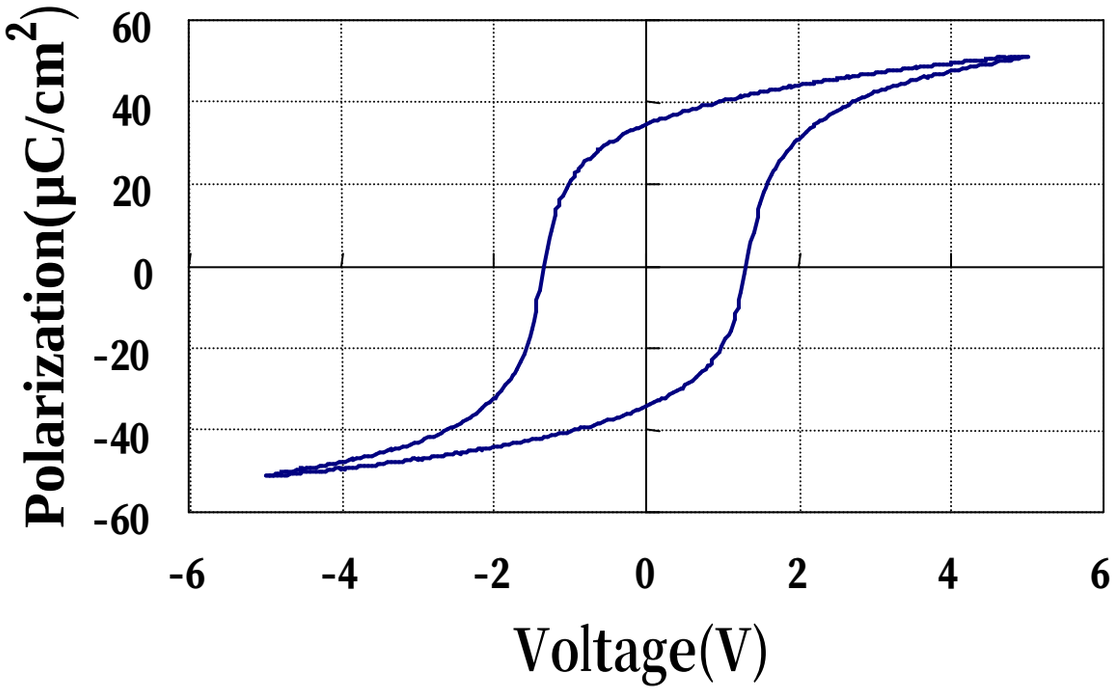
Resistivities of $Ba(Pb_xBi_{1-x})O_3$

- Dependence of crystallization temperature on Bi concentration (x)
- Dependence of Sheet resistance on x

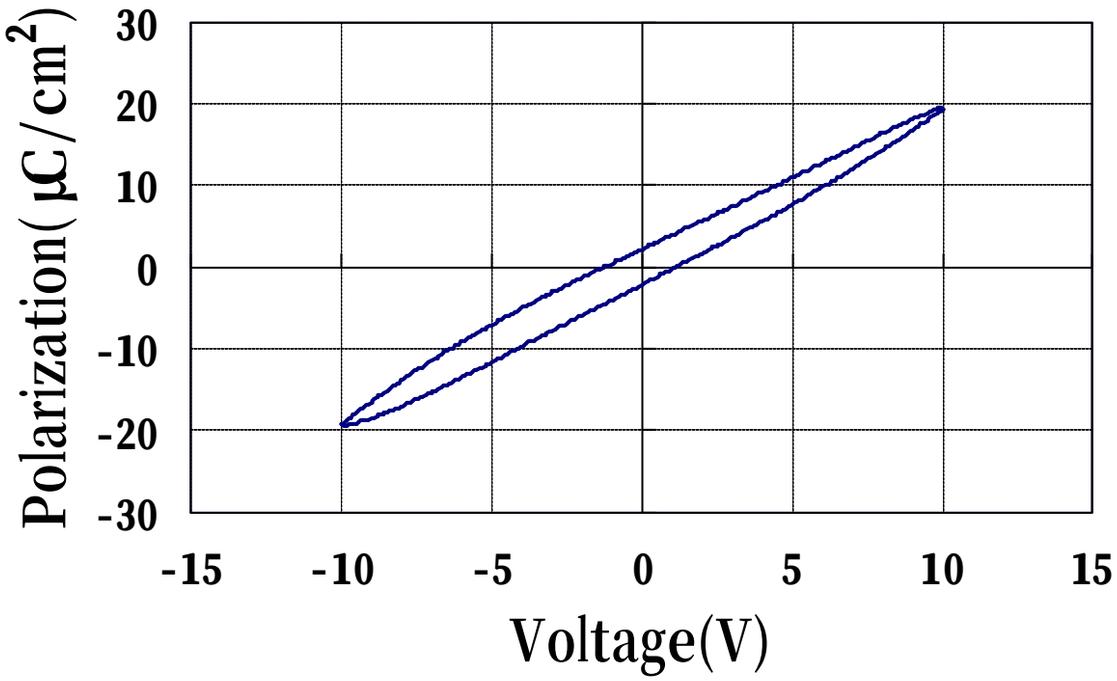
D-E properties of PZT film capacitors annealed in vacuum

Degradation of PZT by deposition of top electrode

- BPO films were prepared at 350℃ of substrate temperature.
- PZT films may be damaged by high temperature in vacuum.



Pt top electrode was prepared at R.T.



at 400℃ → Degradation

D-E properties of Pt/PZT/Pt/TiO_2/Si capacitors

PZT films were damaged by high temperature (>350℃) in vacuum.
→ low process temperature below 350℃

Experimental

Sputtering condition of BBPO films

Preparation Equipment	RF Magnetron Sputter (SPF210H)
Substrate	SiO_2/Si
Depo.Temp	250-500°C
RF Power	100W
Depo.Pres	10-100mTorr
Sputtering Gas	Ar/O_2=50/50
Gas Flow	4sccm
Target-Substrate Space	40mm
Target Composition	$Ba(Bi_xPb_{1-x})_{1.5}$:Powder

Evaluation of BBPO films

- Orientation
  → XRD(θ－2θ)
- Composition
  → XRF
- Sheet resistance
  → 4 probe method
- Hall measurement
  → Van der Pauw methods
- Ferroelectric properties of PZT capacitors (*D*-*E*、Fatigue)
  → TF2000
- Surface morphology
  → AFM

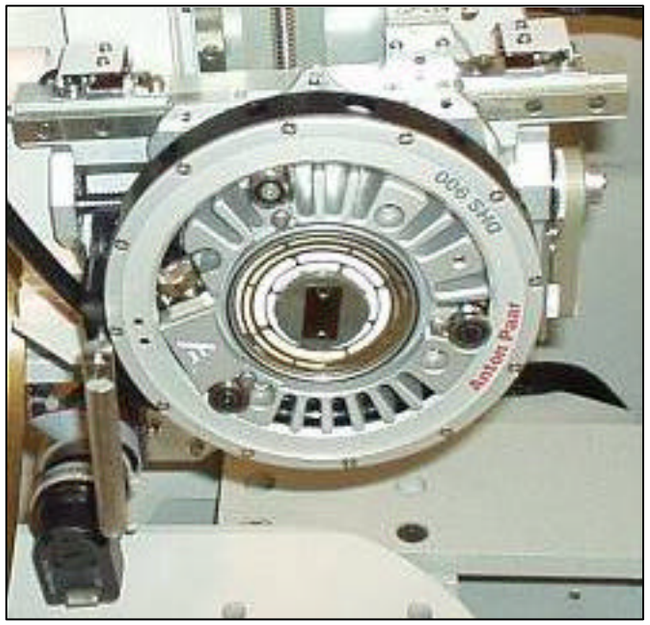
Temperature dependence of XRD

Evaluation of crystallization temperature

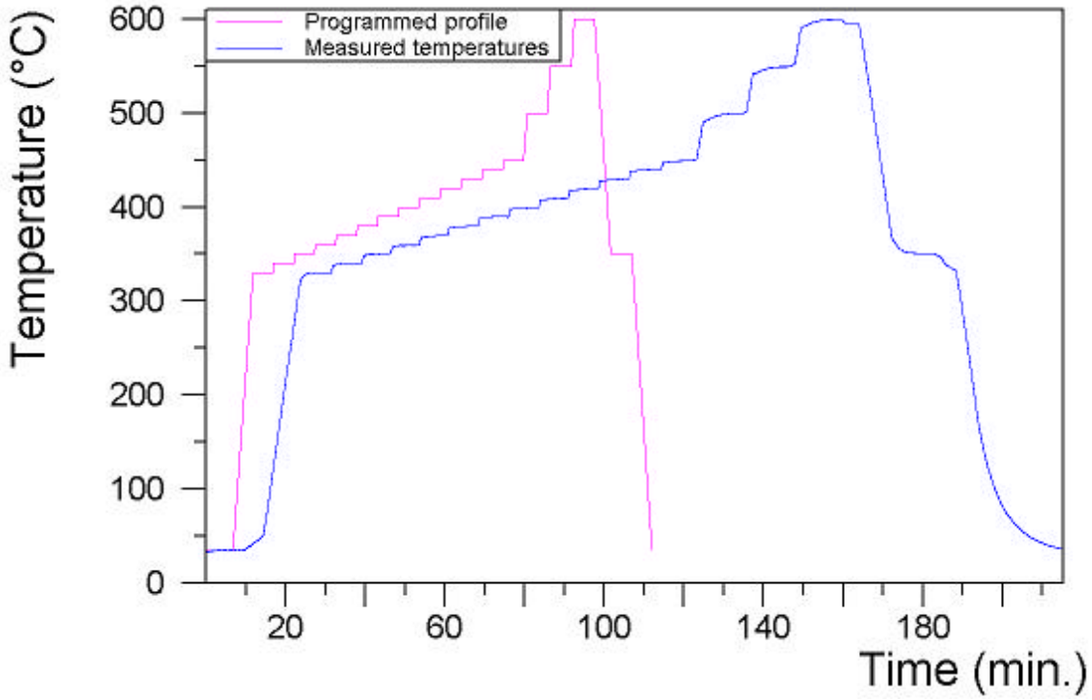
BPBO films were sputtered without substrate heating

⇩

Measurement by XRD with a heater stage

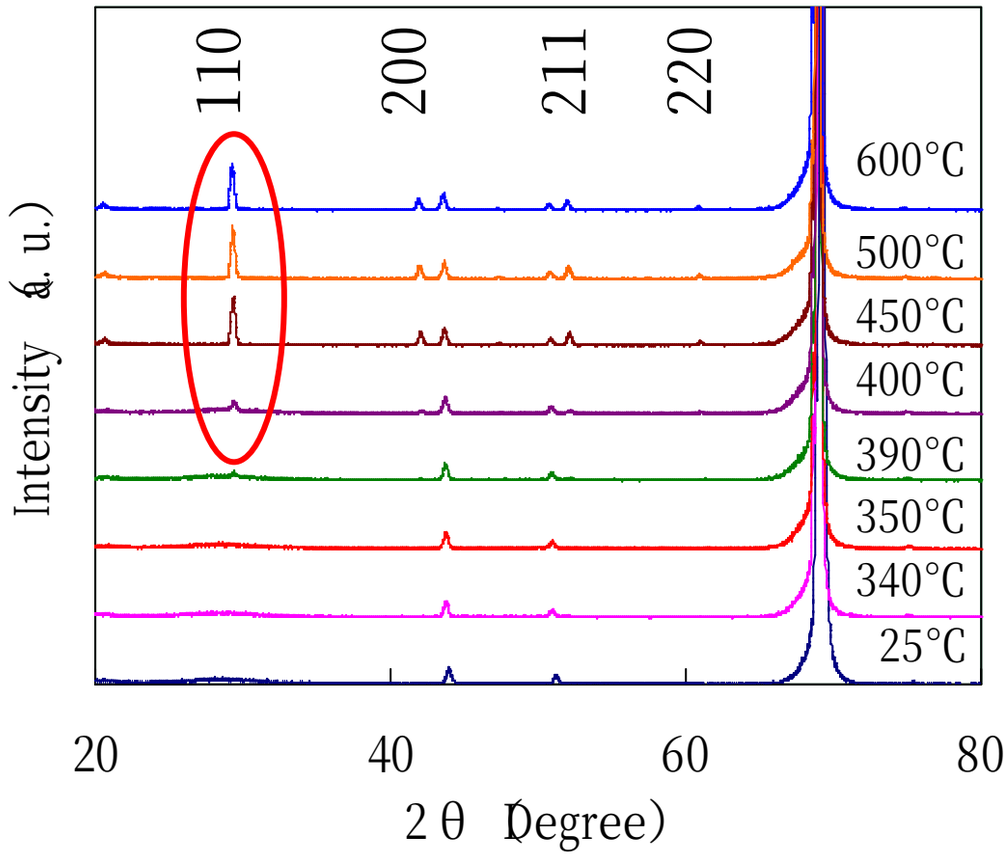


Heater stage of XRD measurement for thin films
(X'Pert DHS900, PANalytical)



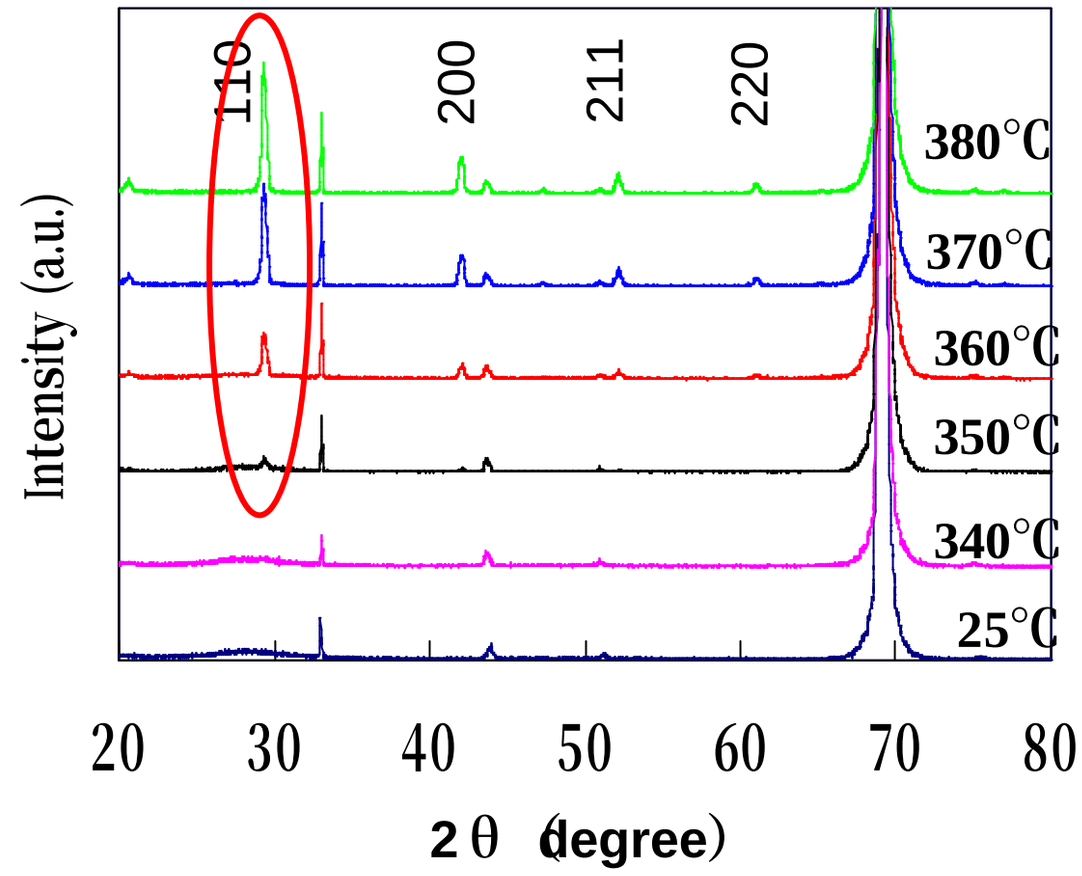
Temperature sequence for XRD measurement
(ΔT=10℃)

Dependence of crystallization temperature on Bi concentration



XRD patterns BPO (x=0%)

Crystallization temperature → 400°C

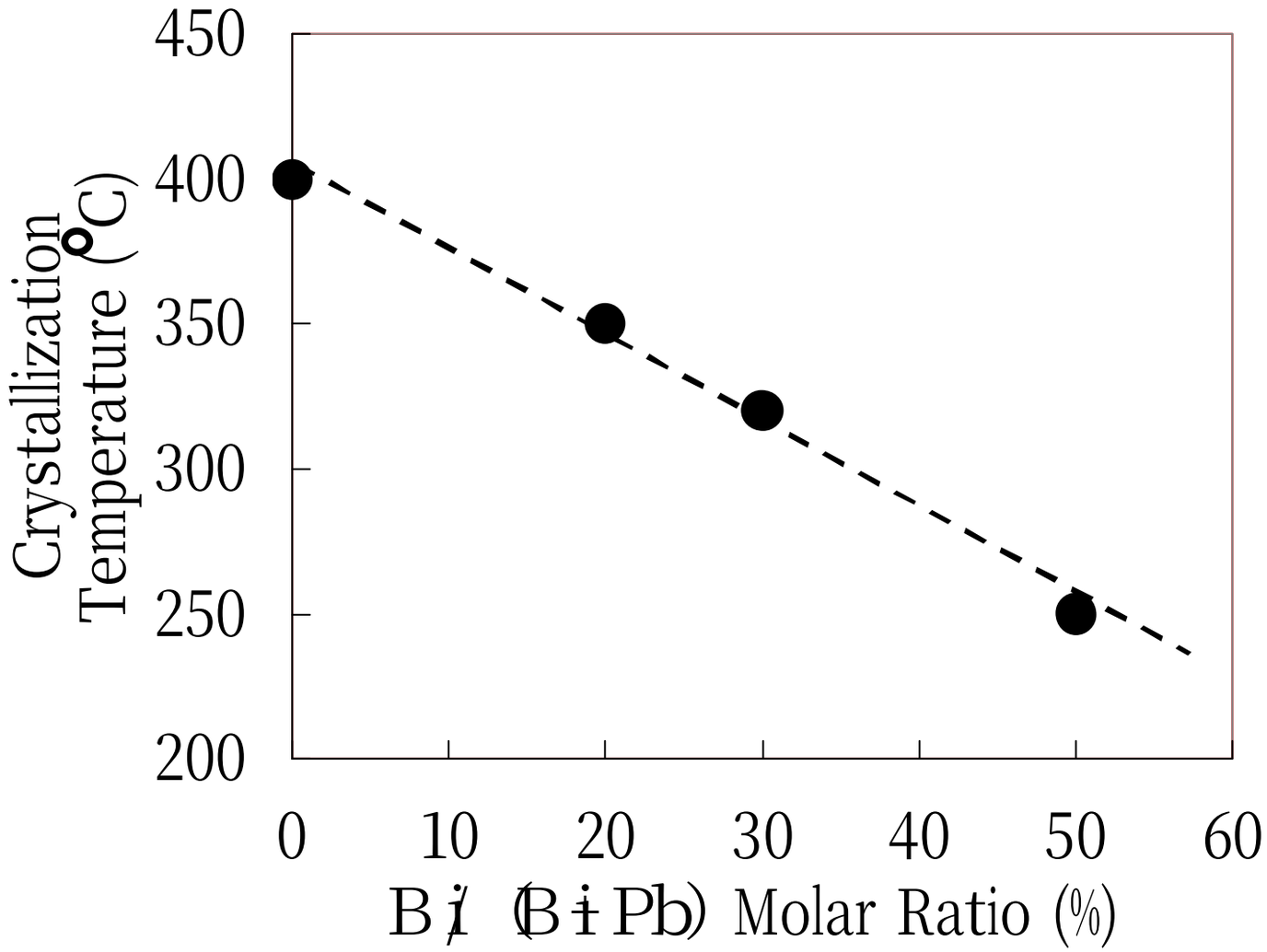


XRD patterns BPBO (x=20%)

Crystallization temperature → 350°C

Crystallization temperature decreased with Bi substitution.

Dependence of crystallization temperature on Bi concentration

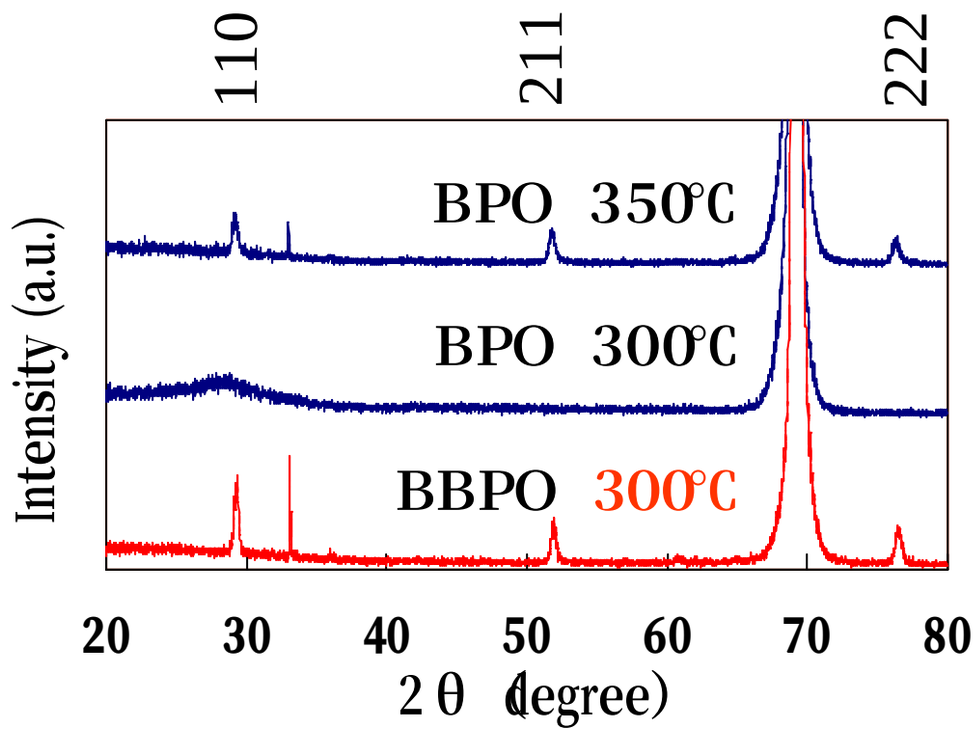


- Temperature decreased above 150℃ with Bi substitution.
- As grown films of Bi/(Bi+Pb)>50% were crystallized due to heating by rf power.

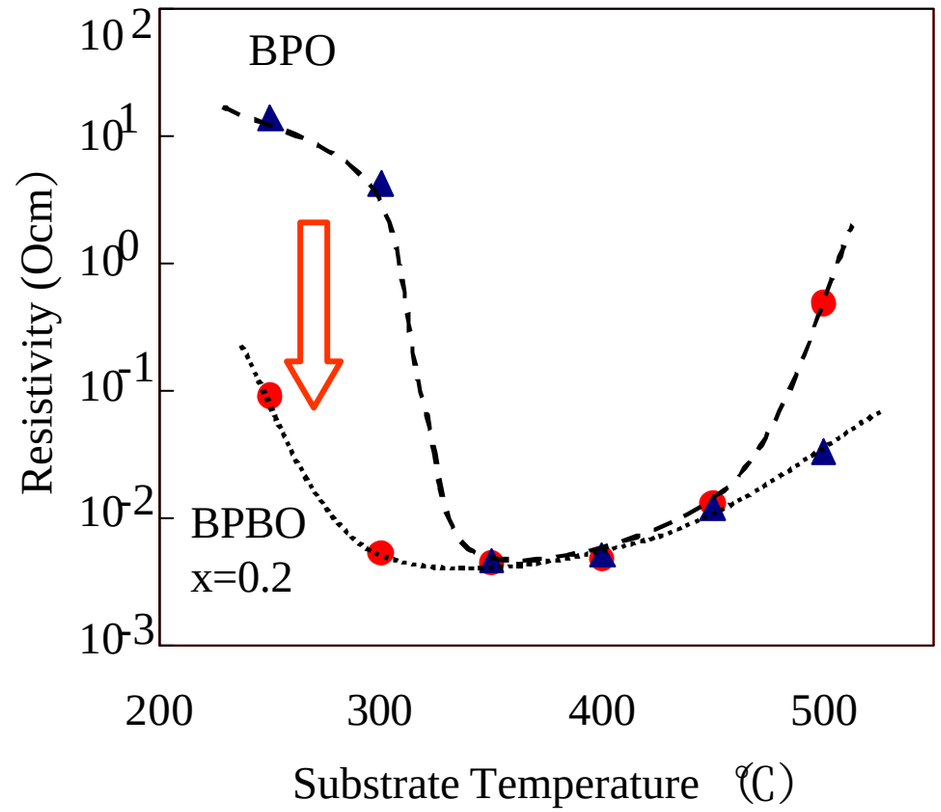
Preparation temperature may be decreased by Bi substitution

Preparation of BPBO films by sputtering with substrate heating

In case of substrate heating



XRD patterns



Sheet resistance

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

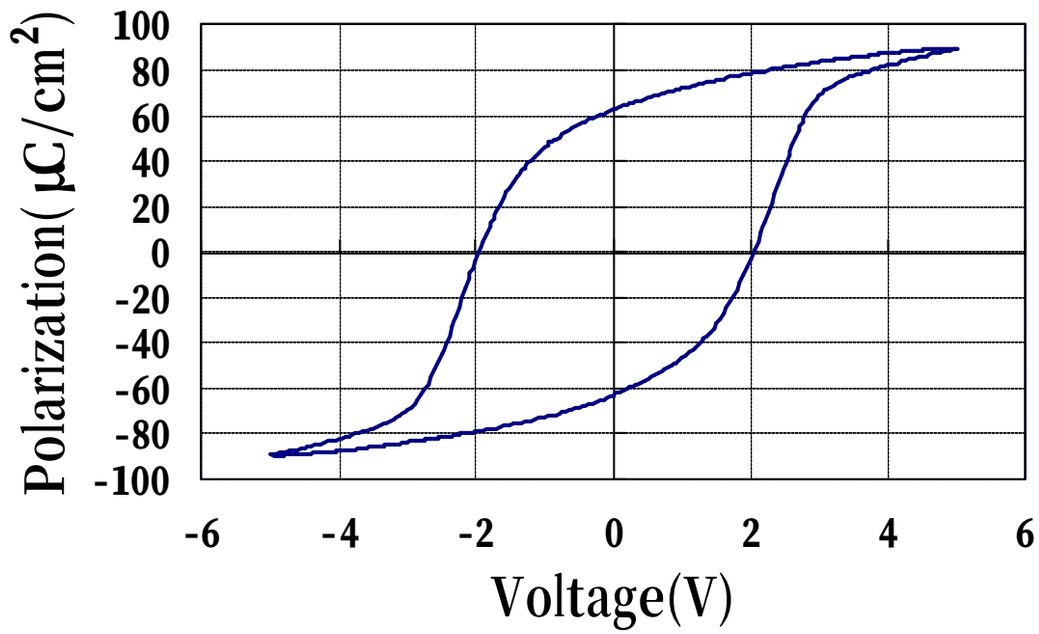
Resistivity at low temperature (250-350℃) can decrease by Bi substitution.

BPO BBPO

4.2 ⇒ 5.3×10^{-3} (Ωcm) at 300℃

Preparation temperature may be decreased by Bi substitution

Ferroelectric Properties of PZT film capacitors using BBPO



D-E hysteresis property of **$Ba(Bi_{0.2}Pb_{0.8})O_3$ /PZT/ $Pt/TiO_2/SiO_2/Si$**

PREPARATION OF $BaPbO_3$ ELECTRODE THIN FILMS BY RF MAGNETRON SPUTTERING AND THEIR PROPERTIES

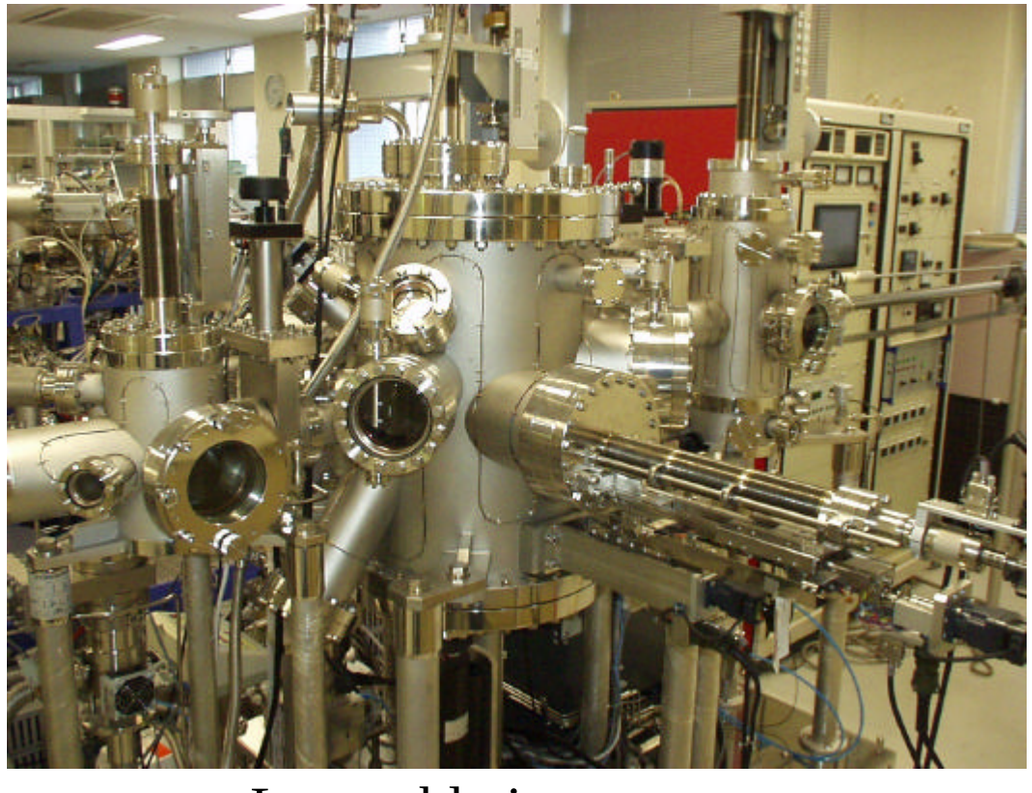
Objective

- 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_2O_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

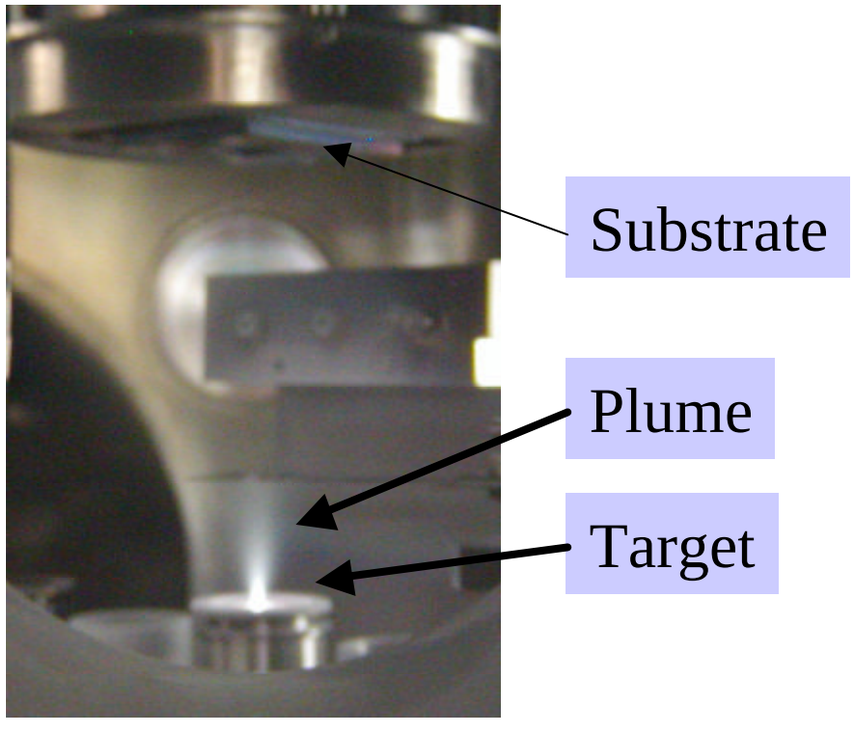
Preparation of BPO films by laser ablation

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



Laser ablation system



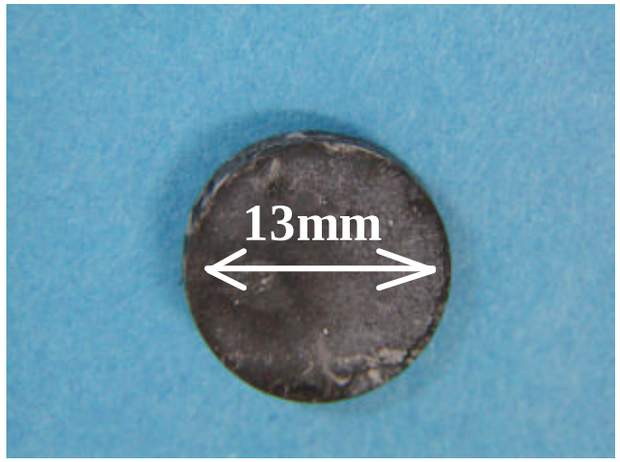
Ablation

Preparation condition of $BaPbO_3$ thin films

Preparation conditions

Substrate Temperature	200 – 550 ℃
Laser	775 nm, 200fs, 1kHz, 0.4W (PA-2001, Clark MXR Inc.)
Deposition Pressure	10 – 70 mTorr
Gas	O_2 100%, 10sccm
Target	Ba : Pb = 1.0 : 1.8
Deposition Time	0 -- 120 min
Substrate-Target Distance	50 mm
Substrate	SiO_2/Si (100)

Laser Ablation : EK-500, Eiko Co.



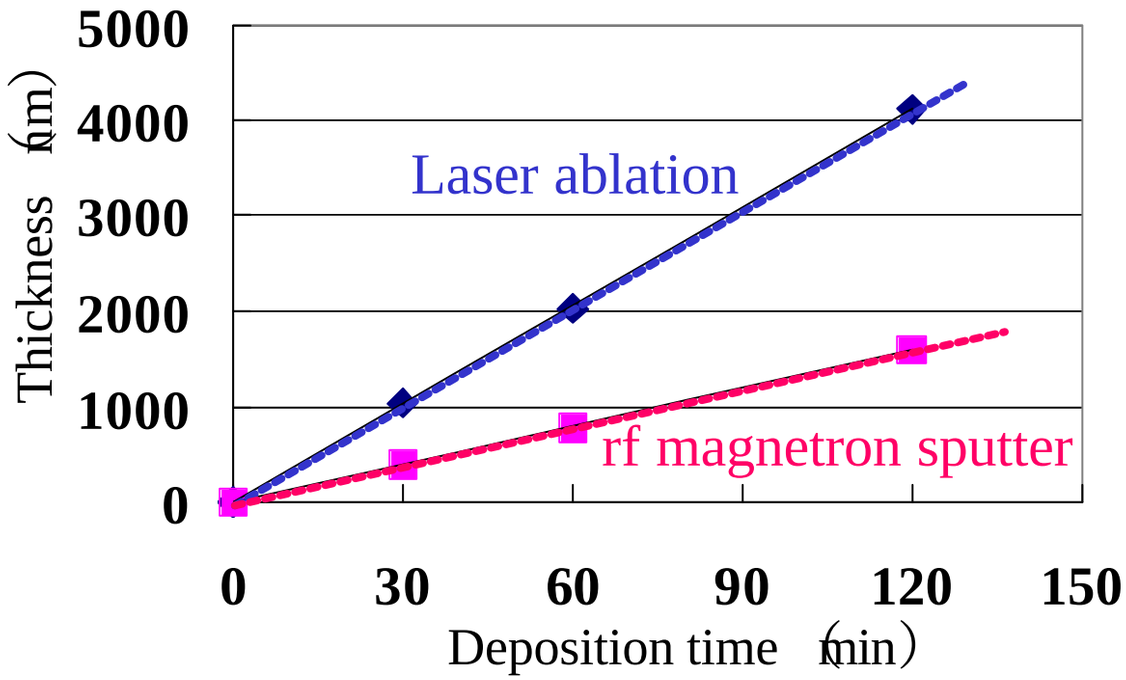
BPO target for laser ablation

850℃ 2h in air

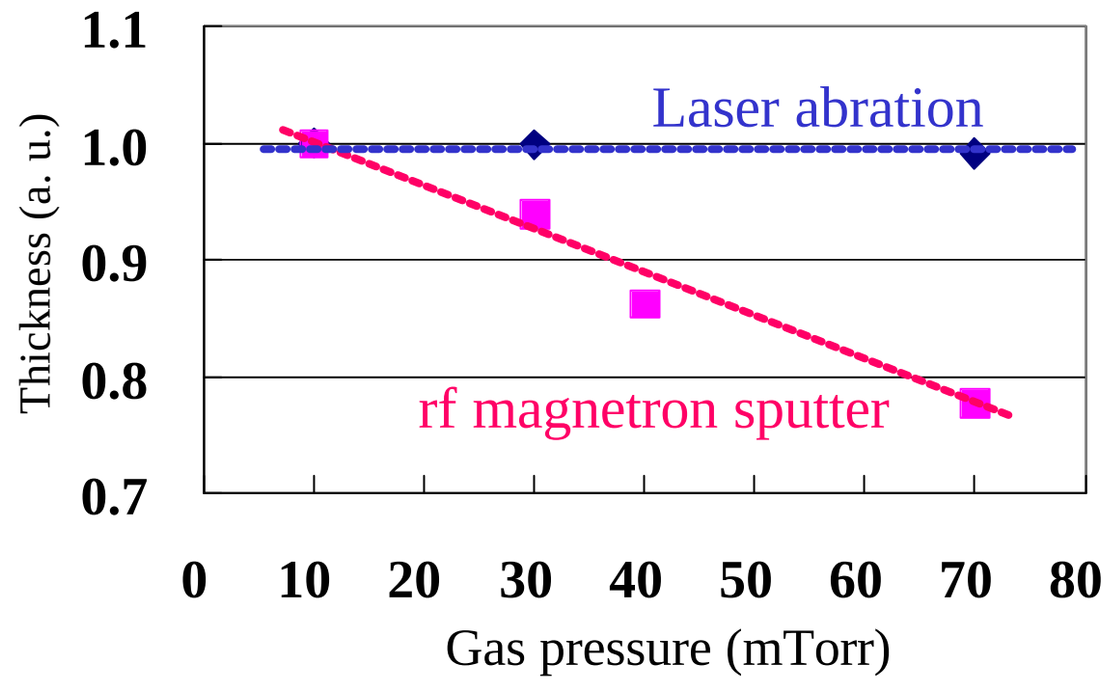
Objective

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

Deposition rate



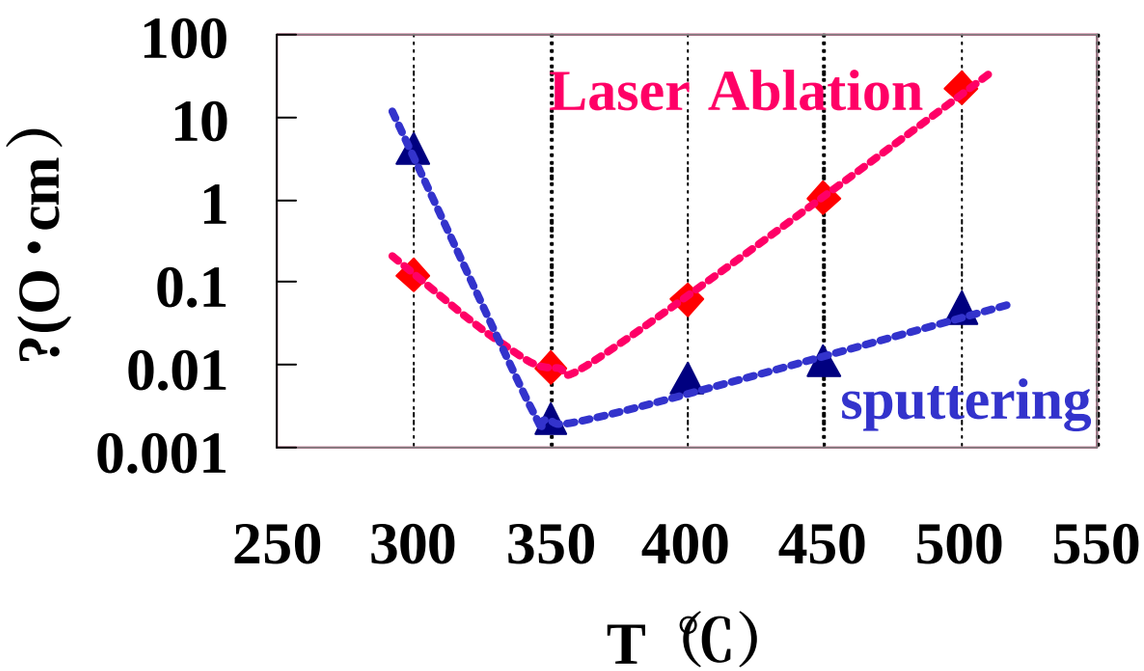
Time dependence of film thickness
(at 350℃, 10 mTorr)



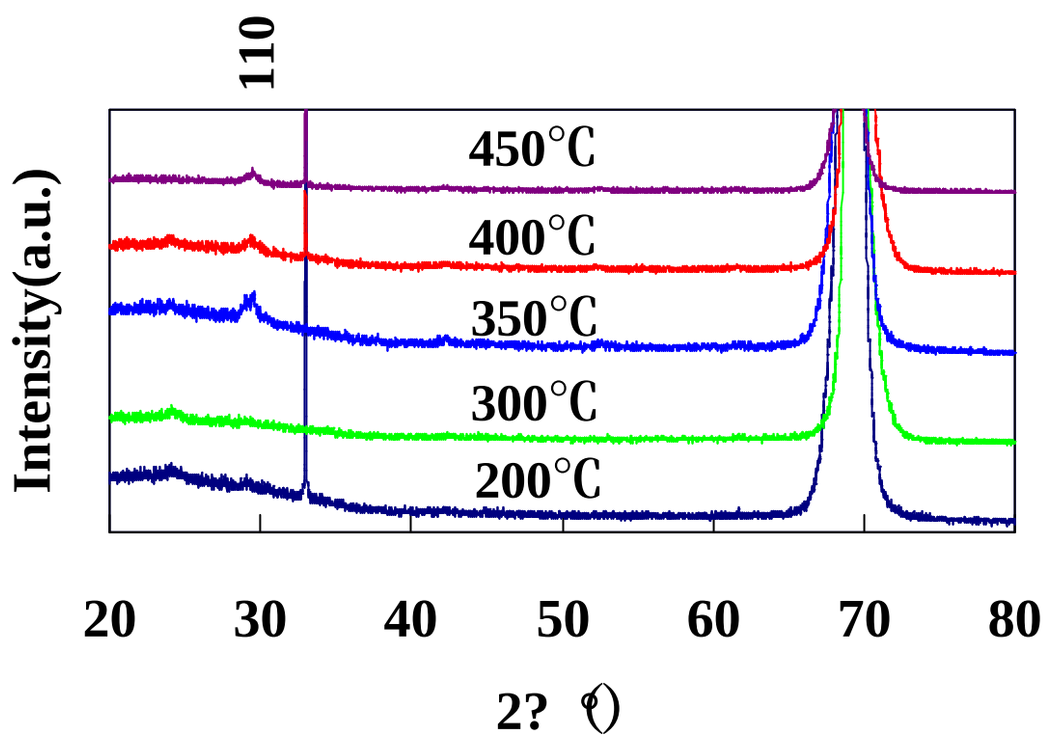
Pressure dependence of film thickness
(at 350℃, 60 min)

- Deposition rate ⇒ 2μm/h
- No dependence on gas pressure

Dependence on substrate temperature



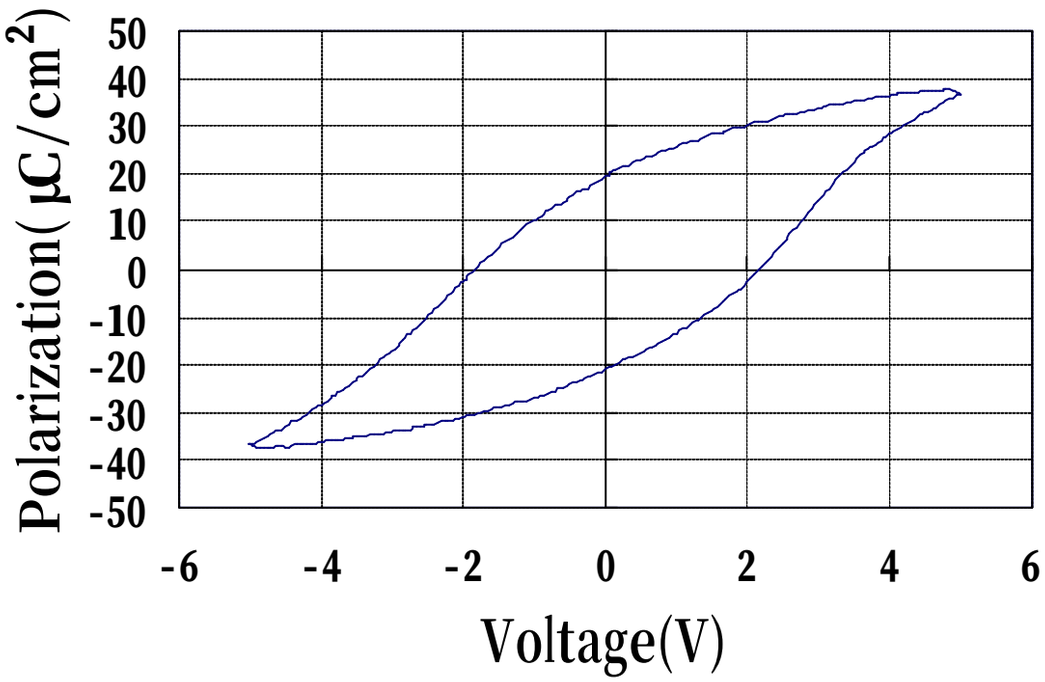
Temperature dependence on resistivity
(Laser: 100Pa, 2h), (Sputter: 10mTorr, Ar:O2=1:1, 100W)



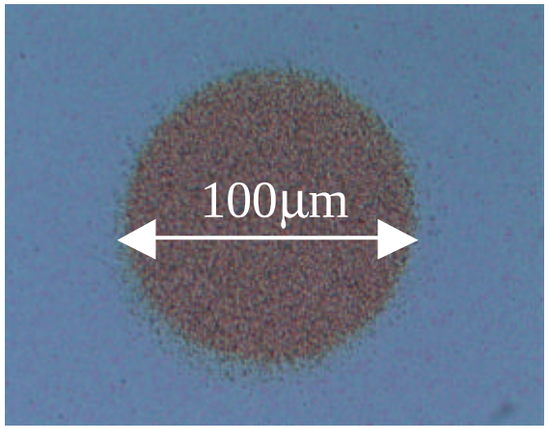
Temperature Dependence of XRD
(Laser: 100Pa, 2h)

- Crystallization temperature of 350℃
- Minimum resistance at 350℃

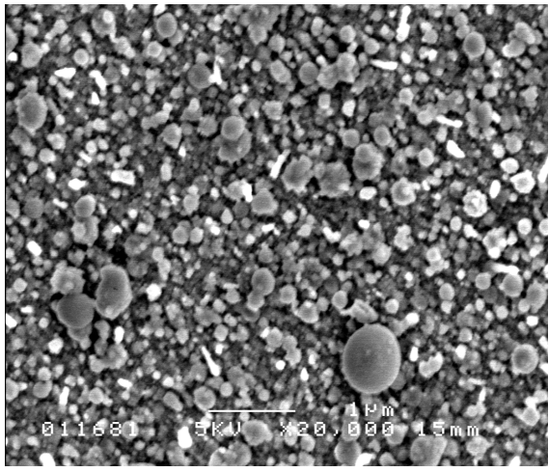
D-E properties of film capacitors with BPO electrode



D-E properties of PZT with BPO top electrodes.
(BPO/PZT/ Pt/TiO_2/SiO_2/Si, 100Pa, 2h, 350℃)



BPO top electrode
(by metal mask method)



1 μm

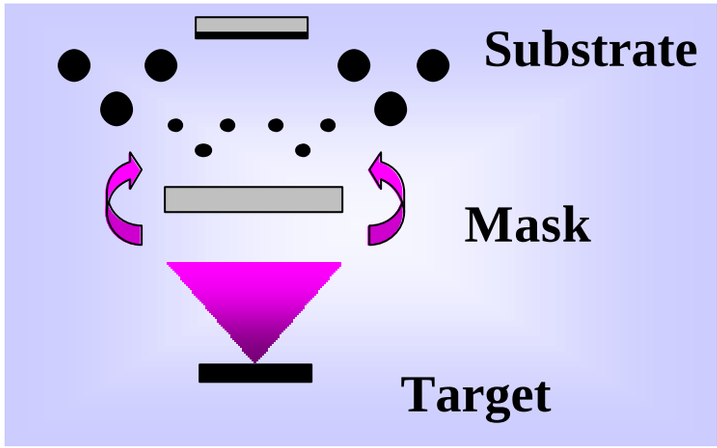
BPO top electrode (SEM)

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

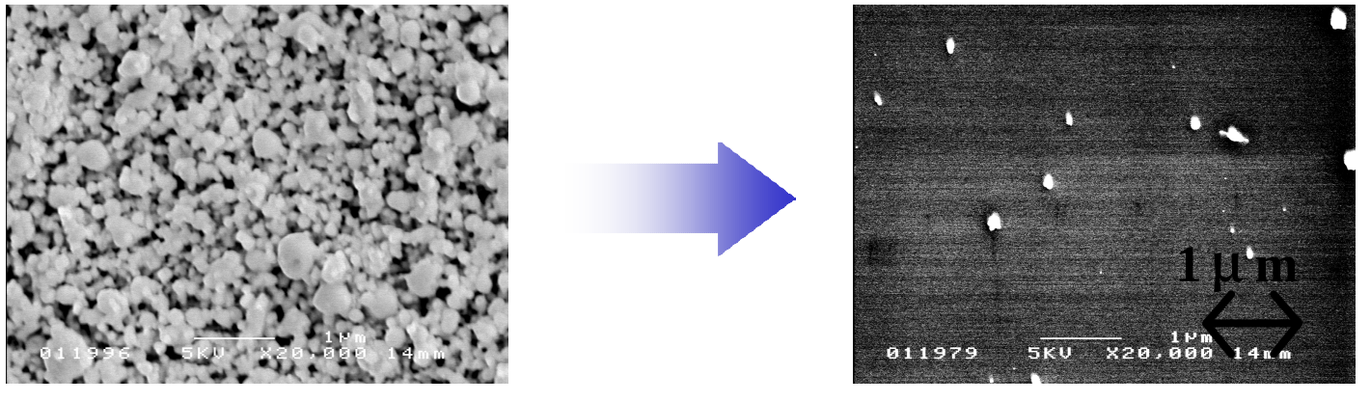
Reduction of droplet formation

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



without mask　　with mask

Influence of mask on surface morphology
(1Pa, 350℃, 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℃～550℃ (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_2O_3(00 •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

Conclusion (2)

- $Ba(Pb_xBi_{1-x})O_3$ (BPBO) film deposition

  ⇒ Low crystallization temperature by Bi substitution (400℃→350℃ at *x*=20%)

  ⇒ BPBO (*x*=20%) was obtained at 300℃ of substrate temperature.

  ⇒ Sheet resistance at low substrate temperature decreased with Bi substitution.

  → Low temperature deposition

- BPO film deposition by laser ablation

  ⇒ Similar preparation condition dependence (perovskite BPO and the minimum resistance were obtained at 350℃)

  ⇒ *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.