

Ferroelectric Properties of Nanoscale PbTiO₃ Films by Hydrothermal Method

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Abstract — Lead (II) nitride (Pb(NO₃)₂), titanium dioxide (TiO₂) and potassium hydroxide (KOH) were used as starting materials. Lead titanate powder was formed by hydrothermal method at 150 C for 6h. The calcium fluoride (CaF₂) and titanium dioxide (TiO₂) were separately adapted as intermediate layer on p-Si (100) substrate. Lead titanate thin film was formed onto CaF₂/Si and TiO₂/Si substrates by spin processor. 100kHz C-V characteristics of PbTiO₃ films were measured by impedance analyzer (LCR meter). Polarization-electric field (P-E) characteristics were measured for both MFIS (Metal/ Ferroelectric/ Insulator/ Semiconductor) structures by applying the same triangular wave electric field in order to allow their application in NVRAM (Non Volatile Ferroelectric Random Access Memory).

Keywords — hydrothermal synthesis, intermediate layer, CaF₂/Si, TiO₂/Si, hysteresis loop

I. INTRODUCTION

Hydrothermal synthesis is a promising method for the manufacture of advanced ceramic powders and thin films. Hydrothermal synthesis can also be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water [1].

The hydrothermal technique has been applied for the synthesis of lead titanate (PbTiO₃ or PT) which is one of the most important ferroelectric materials. The high spontaneous polarization and piezoelectric coefficients, but low aging rate of dielectric constant. The PT-based compound is suitable for a wide range of high temperature and frequency applications [2].

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field. Ferroelectric crystals often show several transition temperatures and domain structure hysteresis, much as do ferromagnetic crystals. The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be

used as a memory function, and ferroelectric capacitors are indeed used to make ferroelectric RAM for computers [3].

II. EXPERIMENTAL PROCEDURE

PbTiO₃ powder was produced by reacting TiO₂ powder with lead nitrate [Pb(NO₃)₂] and alkaline aqueous solution of KOH at 150 C in Teflon-lined stainless steel vessel. Firstly one liter of deionized water (DIW) was poured to 1mol of KOH pellet and stirred slowly to obtain hydrated KOH solution. And then Pb(NO₃)₂, TiO₂ and hydrated KOH solution were mixed in Teflon-lined stainless steel vessel and the mixture was dried at 150 C for 6h. After that, the mixture was cooled down to room temperature and finally PbTiO₃ powder was formed. This hydrothermal synthesized PbTiO₃ powder was operated by ball-milling for 30h to reduce the particle size. To obtain PbTiO₃ sol solution, hydrothermal synthesized PbTiO₃ powder and the appropriate amount of ethylene glycol were used. They were mixed and stirred with magnetic stirrer with constant speed at 600 rpm for 5h to obtain homogeneous PbTiO₃ sol solution. The suitable amount of ethylene glycol was separately mixed with TiO₂ and CaF₂ powders to get TiO₂ and CaF₂ solution for intermediate layers.

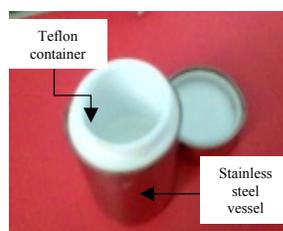


Fig 1. Teflon-lined stainless steel bomb

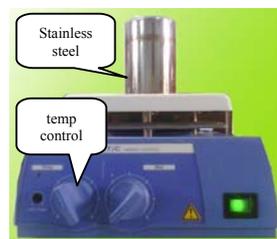


Fig 2. Hydrothermal synthesis of PbTiO₃

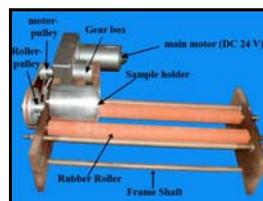


Fig 3. Photograph of ball-milling

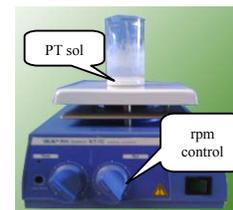


Fig 4. Magnetic stirrer with heat controller

A. Substrate preparation

Defect-free and polished p-Si (100) (1cm x 1cm) wafer was used as a substrate. To get the naked surface and to remove the contamination, ultrasonic cleaning process was made as follows:

- the Si wafer was washed in boiling acetone (60°C), then in boiled propanol (50°C) for 5 min to remove greasy film.
- it was immersed in nitric acid HNO₃ for 3 min in order to remove ionic contamination.
- it was etched in buffered hydrofluoric acid (34.6% NH₄F: 6.8% HF: 58.6% H₂O) for 2 min to remove oxide film.
- it was cleaned in DIW and dried on flat-oven at 100°C in a few minute.
- finally, it was purged with N₂ gas and clean Si-wafer was formed.

B. Thin film deposition (single wafer spin processor)

Intermediate layers (TiO₂ & CaF₂) were formed on p-Si (100) substrate (1cm x 1cm) by using single wafer spin processor. TiO₂/Si and CaF₂/Si layers were dried at 400°C for 1h. PbTiO₃ sol solution was also deposited onto both substrates (TiO₂/Si & CaF₂/Si) by single wafer spin processor. The substrate was placed on fragment adapter and the PbTiO₃ sol solution was poured onto substrate. The spin speed or rotational speed was set 4000 rpm and spinning time was 30 s. To change the sol coating into oxide film, they were annealed at 500°C in O₂-atm for 1h respectively. Finally, PbTiO₃/TiO₂/Si and PbTiO₃/CaF₂/Si cells were formed.

C. Design consideration

In order to get Ni-conductive layer, the exposed area (0.3cm x 0.3cm) for front side and (0.5cm x 0.5cm) for back side were set and remaining area was covered with mask. And then the film was immersed in Ni solution. After 5 min, it was taken from Ni-solution and dried at room temperature. After removing the mask, Ni-conductive layer was formed. Cu-wire was soldered on front and counter conductive layer. The structure of MFIS with electrode was shown in Fig 5.

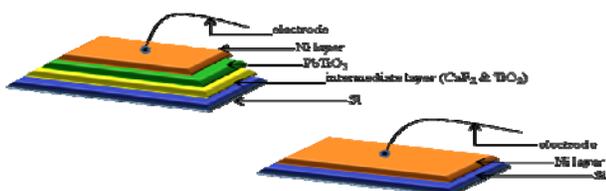


Fig 5. Structure of MFIS (front & back side)

III. RESULTS AND DISCUSSION

A. XRD analysis

The structures of crystallized films were examined by XRD analysis. The sample was scanned over the range 10 to 70 at a scan rate of 0.02 /0.12s. The obtained XRD pattern was analyzed by using PROSZKI software package and the diffraction peaks were indexed. The structural properties of PbTiO₃ powder was shown in Fig 6. The XRD pattern was totally matched with standard library file of #70-0746>PbTiO₃

lead titanate oxide and it showed that the hydrothermal synthesized PbTiO₃ powder were formed at a low temperature. The lattice distortion and crystallize size of PbTiO₃ were 1.058 and 29.6nm. The structures of TiO₂/Si and CaF₂/Si films could be identified and indicated in Fig.7(a&b). Both XRD patterns were good agree with the JCPDS files of #89-4921>anatase,syn-TiO₂ and #89-4794>Fluorite CaF₂. It was found that the intermediate layers of TiO₂ and SiO₂ were formed on Si substrates. The structural properties of PbTiO₃/TiO₂/Si and PbTiO₃/CaF₂/Si films were also investigated and shown in Fig.8(a&b). These two patterns were matched with the reference profiles of # 48-0105>PbTiO₃-lead titanate oxide and #06-0452>Macedonite,syn-PbTiO₃. All peaks were well consistent with the respective library files. The most dominant peak was (323) reflection (2θ=31.78) and (002) reflection (2θ=44.26) for PbTiO₃/TiO₂/Si and PbTiO₃/CaF₂/Si films. According to this information, hydrothermal PbTiO₃ was tetragonal symmetry. They were occurred at the corresponding Bragg's angle about 31.78 and 44.26 . To obtain the crystallize size from XRD, we applied Debye-Scherrer formula and they were evaluated to be 14.3nm and 39.8nm for respective cells at FWHM of 0.576 and 0.215 . The maximum degree of FWHM was found at PbTiO₃/TiO₂/Si cell structure. The peak broadening could be related to the distortion of the host lattice, which was presumably due to large strain induced effect of the anatase TiO₂. The largest crystallite size was observed at PbTiO₃/CaF₂/Si cell. The increase of crystallite size was ascribed to the nice crystal growth after completion of the Pb(NO₃)₂ and KOH base. The lattice strains were also found to be 1.20 and 1.14 for both cells.

TABLE I
LATTICE STRAINS AND CRYSTALLIZE SIZES OF STANDARD PBTIO₃, HYDROTHERMAL SYNTHESIZED PBTIO₃ POWDER AND FILMS

Sample	c/a	Crystallize size(nm)
Standard PbTiO ₃	1.063	-
Hydrothermal PbTiO ₃	1.058	29.6
PbTiO ₃ /TiO ₂ /Si	1.200	14.3
PbTiO ₃ /CaF ₂ /Si	1.144	39.8

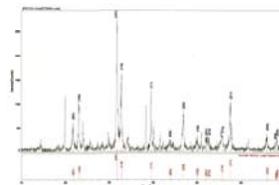


Fig 6. XRD pattern of hydrothermal synthesized PbTiO₃ powder

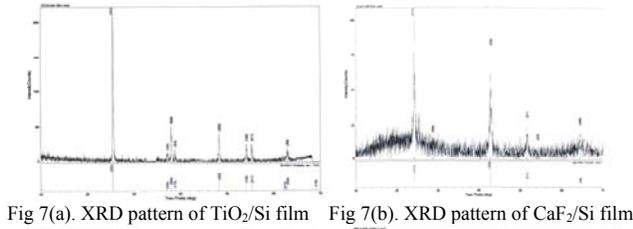


Fig 7(a). XRD pattern of TiO₂/Si film Fig 7(b). XRD pattern of CaF₂/Si film

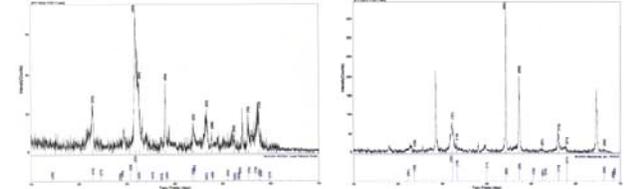


Fig 8(a). XRD pattern of PbTiO₃/TiO₂/Si film Fig 8(b). XRD pattern of PbTiO₃/CaF₂/Si film

B. Nanoscale hydrothermal synthesized PbTiO₃ powder (SEM analysis)

The microstructural properties of hydrothermal synthesized PbTiO₃ powder were observed by SEM analysis. The grain sizes were measured by using well known bar code system. Bar code size was 200nm with magnification of 24.7k. Working distance was about 6.5mm. The average grain size of hydrothermal PbTiO₃ powder was found to be about 50nm to 70 nm in diameter. This value was within the range of accepted value for the nanotechnology. Some pores and grain growth pattern were occurred among the crystalline grains. According to the small grain size, relatively high density was found on the micrograph.

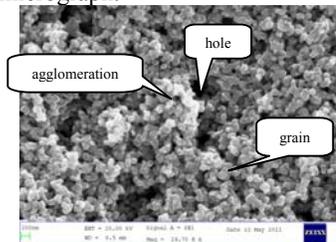


Fig 9. SEM micrograph of hydrothermal PbTiO₃ powder

C. Nano films of hydrothermal synthesized PbTiO₃ (SEM analysis)

SEM micrographs of TiO₂/Si and CaF₂/Si films were shown in Fig.10(a&b). Fig 11.(a&b) indicated the SEM micrographs of PbTiO₃/TiO₂/Si and PbTiO₃/CaF₂/Si films. It was found that all films were crack-free and showed uniform grain distribution except the film of PbTiO₃/CaF₂/Si. The grains were agglomerated and had average size of 76nm, 80nm, 90nm and 95nm in diameter for respective films. It was revealed that the grain sizes in PbTiO₃ deposited films were greater than that of non- deposited films. It was also observed that some holes were formed in the CaF₂ intermediate layered films. Right orientation was occurred in CaF₂/Si film and others were left oriented. Grain growth patterns were formed among the crystalline grains.

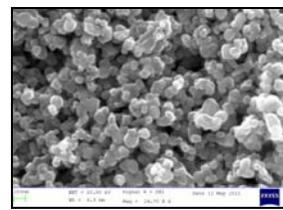


Fig 10(a) SEM micrograph of TiO₂/Si film

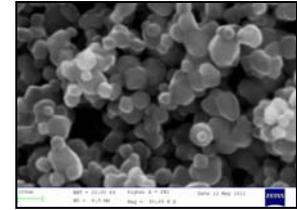


Fig 10(b) SEM micrograph of CaF₂/Si film

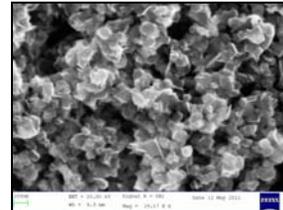


Fig 11(a).SEM micrograph of PbTiO₃/TiO₂/Si film

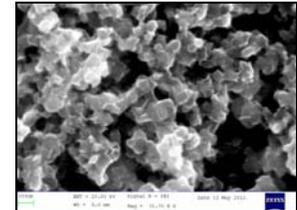


Fig 11(b).SEM micrograph of PbTiO₃/CaF₂/Si film

D. C-V characteristics

In order to examine the ferroelectricity and memory behaviour of hydrothermal synthesized films, measurements were carried out by using Impedance Analyzer (QuadTech:1730) at applied frequency of 100kHz. The bias voltage was applied for the range from -5V to +5V. At -5V, the capacitance developed a depletion layer under the gate and therefore it had finite capacitance reducing the device capacitance. The capacitance cycled counterclockwise, which were consistent with a polarization switching mechanism and contrary to the hysteresis developed by charge injection. On C-V curve, the voltage gap was significantly formed and it might be due to the non-volatile memory nature of film. The hysteresis gap, the memory window (MW) was measured on C-V curve and it was found to be 0.80V and 0.75V for both films. The threshold voltage and flat-band voltage occurred at sweep up and down directions (voltage increasing & decreasing directions) were measured on C-V curves. The measured values for both devices were collected and listed in Table 2.

TABLE II
MW, V_{TH,U}, V_{TH,D}, V_{FB,U} AND V_{FB,D} OF PBTIO₃/TIO₂/SI AND PBTIO₃/CAF₂/SI FILMS

Sample	MW (V)	V _{TH,U} (V)	V _{TH,D} (V)	V _{FB,U} (V)	V _{FB,D} (V)
PbTiO ₃ /TiO ₂ /Si	0.80	2.00	1.25	-1.37	-2.60
PbTiO ₃ /CaF ₂ /Si	0.75	1.75	1.00	-1.10	-1.88

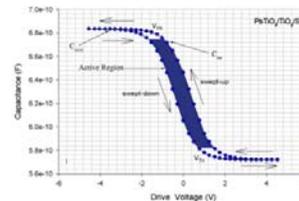


Fig 12(a) C-V characteristic of PbTiO₃/TiO₂/Si film

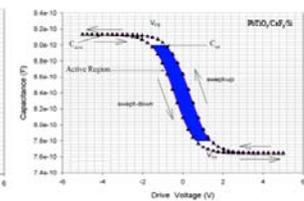


Fig 12(b) C-V characteristic of PbTiO₃/CaF₂/Si film

E. Hysteresis characteristics

Ferroelectricity and non-volatility of hydrothermal synthesized films were interpreted by means of P-E hysteresis loop. Hysteresis loop measurements were performed with Sawyer-Tower circuit without pooling treatment at 100kHz. The generated loop was recorded on oscilloscope (YOKOGAWA ALS10 50MHz) in which the film was served as circuit element. The hysteresis loops of PbTiO₃/TiO₂/Si and PbTiO₃/CaF₂/Si films were shown in Fig 13.(a&b). Both hysteresis loops looked non-linear and slim. The remanent polarization density (P_r) values were 39.5 μC/cm² and 35.1 μC/cm². The spontaneous polarization densities were 49.2 μC/cm² and 48.0 μC/cm² for both films. Table 3. described the P_r, P_s and E_c values for both fabricated cells.

TABLE III
2P_r, P_r, P_s, DIFFERENCE BETWEEN P_s & P_r AND E_c VALUES FOR
PBTiO₃/TiO₂/SI AND PBTiO₃/CAF₂/SI FILMS

Sample	P _r (μC/cm ²)	P _s (μC/cm ²)	E _c (kV/cm)
PbTiO ₃ /TiO ₂ /Si	39.5	49.2	1.4
PbTiO ₃ /CaF ₂ /Si	35.1	48.0	1.2

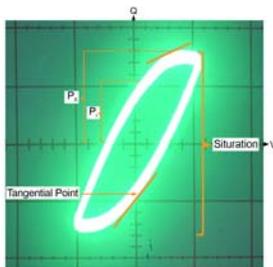


Fig 13(a) P-E hysteresis loop for PbTiO₃/TiO₂/Si film

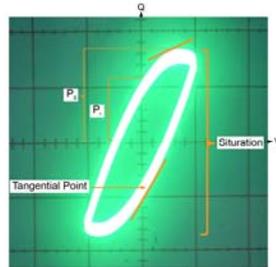


Fig 13(b) P-E hysteresis loop for PbTiO₃/CaF₂/Si film

IV. CONCLUSION

Hydrothermal synthesis PbTiO₃ powder was successfully formed at a low temperature. The grain size of hydrothermal synthesized PbTiO₃ powder was found to be about 50nm-70nm in diameter. The grain sizes of intermediate layers (TiO₂/Si and CaF₂/Si) were evaluated to be 76nm and 80nm.

The average grain sizes were also found about 90nm and 95nm in diameter for hydrothermal synthesized PbTiO₃/TiO₂/Si and PbTiO₃/CaF₂/Si films. These values were within the range of accepted value for the nanotechnology.

From the C-V and hysteresis loop characteristics, it was clearly found that both films showed the memory behavior and it could be used as non volatile ferroelectric random access memory. They were satisfied the essential requirement for the development of MFIS. Nowadays DRAM (Dynamic Random Access memory) such as DDR, DDR2 and DDR3 (Double Date-Rate Random Access Memory) has been used for computer memory. They are made of dielectric materials and can be volatile. FeRAM (Ferroelectric Random Access Memory) is composed of ferroelectric materials and it can be used as non volatile ferroelectric random access memory. According to the results obtained, the fabrication technique and measurement system were of low cost and environmentally friendly. The hydrothermal synthesis was found to be low temperature synthesis.

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