Hydrothermal Synthesis of Nano-sized PbTiO3 Powder and Epitaxial Film for Memory Capacitor Application

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Abstract

Hydrothermal synthesized lead titanate powder was prepared in a Teflon-lined stainless steel bomb. Calcium fluoride (CaF2) and titanium dioxide (TiO2) were separately adapted as intermediate layers on p-Si (100) substrates. The microstructures of TiO2 and CaF2 layers were examined by FESEM. Lead titanate (PbTiO3) film was formed on both the CaF2/Si and TiO2/Si structures using the spin coating technique. FESEM images revealed the nano-sized grain morphology of PbTiO3 films. C-V characteristics were measured and good hysteresis nature was formed for both MFIS structure of the film. The Sawyer-Tower circuit was also used to look at the P-E hysteresis loop of both MFIS cells. The loop of PT/TiO2/Si was wider than that of PT/CaF2/Si cell. Also, the higher value of polarization (Ps=49.2 µC/cm2) for PT/TiO2/Si could be explained on the basis of higher dipole moment in this TiO2 buffer layer.

Keywords: Hydrothermal synthesis, nano-sized PbTiO3 powder, C-V characteristics, hysteresis loop

1. Introduction

Hydrothermal synthesis is a promising method for the manufacturing of advanced ceramic powders and thin films. Hydrothermal synthesis can also be defined as a synthesis method for single crystals that depends on the solubility of minerals in hot water under high pressure (Chien et al., 1999). The hydrothermal technique has been applied to the synthesis of lead titanate (PbTiO3 or PT) which is one of the most important ferroelectric materials, with 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 temperatures and frequency applications (Chankaew and Rujiwatra, 2010). Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field. 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 (Tokumitsu et al., 2001; Yoon and Ishiwara, 2001; Li et al., 2002; Suzuki and Tokumitsu, 2002). T. Morita and Y. Cho
reported that the remanent polarization for lead titanate was to be 81\(\mu\)C/cm\(^2\) (Morita and Cho, 2005).

2. Experimental Procedure

2.1 Preparation of PbTiO\(_3\) powder and solution

PbTiO\(_3\) powder was produced by reacting TiO\(_2\) powder with lead nitrate [Pb(NO\(_3\))\(_2\)] and alkaline aqueous solution of KOH at 120\(^\circ\)C in Teflon-lined stainless steel vessel. Firstly Pb(NO\(_3\))\(_2\), TiO\(_2\) and 1mol of KOH solution were mixed in Teflon-lined stainless steel vessel and the mixture was dried at 120\(^\circ\)C for 6h. After that, the mixture was cooled down to room temperature and finally PbTiO\(_3\) powder was formed. This hydrothermal synthesized PbTiO\(_3\) powder was operated by ball-milling for 30h to reduce particle size. To obtain PbTiO\(_3\) sol solution, hydrothermal synthesized PbTiO\(_3\) powder and the appropriate amount of ethylene glycol were used. They were mixed and stirred with a magnetic stirrer at a constant speed of 600 rpm for 5h to obtain homogeneous PbTiO\(_3\) sol solution. The suitable amount of ethylene glycol was separately mixed with TiO\(_2\) and CaF\(_2\) powder to get TiO\(_2\) and CaF\(_2\) solution for intermediate layers.

2.2 Thin film deposition

Defect-free and polished p-Si (100) (1cm x 1cm) wafer was used as a substrate. An ultrasonic cleaning process was done to get the naked surface and remove contamination. Intermediate layers (TiO\(_2\) & CaF\(_2\)) were formed on p-Si (100) substrate (1cm x 1cm) by using a single wafer spin processor (WS-400BZ-6NPP/LITE). TiO\(_2\)/Si and CaF\(_2\)/Si layers were dried at 400\(^\circ\)C for 1h. PbTiO\(_3\) sol solution was also deposited on both substrates (TiO\(_2\)/Si & CaF\(_2\)/Si) by single wafer spin processor. The substrate was placed on fragment adapter and the PbTiO\(_3\) sol solution was poured onto substrate. The spin speed or rotational speed was set at 4000 rpm and spinning time was 30s. To change the sol coating into oxide film, they were annealed at 500\(^\circ\)C in O\(_2\)-atm for 1h respectively. Finally, PbTiO\(_3\)/TiO\(_2\)/Si and PbTiO\(_3\)/CaF\(_2\)/Si cells were obtained.

2.3 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 the front and counter-conductive layers.

3. Results and Discussion

3.1 XRD analysis

The structures of crystallized films were examined by XRD analysis and shown in Fig 1. The XRD pattern was totally matched with standard library file of #70-0746>PbTiO\(_3\) lead titanate oxide and it showed that the hydrothermal synthesized PbTiO\(_3\) powder were formed at a low temperature. The lattice distortion and crystal size of PbTiO\(_3\) were 1.058 and 29.6nm respectively. The structures of TiO\(_2\)/Si and CaF\(_2\)/Si films could be identified and indicated in Fig 2(a-b). Both XRD patterns agreed well with the standard JCPDS and it showed that the intermediate layers of TiO\(_2\) and SiO\(_2\) were formed on Si substrates. The structural properties of PbTiO\(_3\)/TiO\(_2\)/Si and
PbTiO3/CaF2/Si films were also investigated and shown in Fig 3(a-b). The crystal sizes were evaluated to be 14.3nm and 39.8nm for PbTiO3/TiO2/Si and PbTiO3/CaF2/Si films, respectively. 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 increase of crystal 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.
3.2 Nanoscale hydrothermal synthesized PbTiO3 films (SEM analysis)

Fig 4(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 porous. The grains were agglomerated and had average sizes of 80nm and 85nm in diameter for respective films. Grain growth patterns were formed among the crystalline grains.

![SEM micrographs of (a) PbTiO3/TiO2/Si film and (b) PbTiO3/CaF2/Si film](image)

3.3 C-V characteristics

In order to examine the ferroelectricity and memory behaviour of hydrothermal synthesized films, measurements were carried out using an 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 device capacitance. The capacitance cycled counterclockwise, 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.

![C-V characteristics for (a) PbTiO3/TiO2/Si film and (b) PbTiO3/CaF2/Si film](image)
3.4 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 a Sawyer-Tower circuit without pooling treatment at 100kHz. The generated loop was recorded on an oscilloscope (YOKOGAWA ALS10 50MHz) in which the film served as circuit element. The hysteresis loops of PbTiO3/TiO2/Si and PbTiO3/CaF2/Si films were shown in Fig 6(a-b). Both hysteresis loops looked non-linear and slim. The remanent polarization density (Pr) values were 39.5µC/cm² and 35.1µC/cm². The spontaneous polarization densities were 49.2 µC/cm² and 48.0 µC/cm² for both films. The hysteresis loops were well developed, confirming their Fe nature. The higher value of Ps & Pr can be explained on the basis of higher dipole moment in this temperature. Moreover, the domain growth in PbTiO3/TiO2/Si film showed easier given the fact that it has higher ε with low cost.

![Fig 6. P-E hysteresis loops of (a) PbTiO3/TiO2/Si film and (b) PbTiO3/CaF2/Si film](image)

4. Conclusion
Hydrothermal synthesis PbTiO3 powder was successfully formed at low temperature. The grain size of hydrothermal synthesized PbTiO3 powder was found to be about 50nm-70nm in diameter. The average grain sizes were also found about 80nm and 85nm in diameter for hydrothermal synthesized PbTiO3/TiO2/Si and PbTiO3/CaF2/Si films. These values were within the range of accepted values for the nanotechnology. From the C-V and hysteresis loop characteristics, it was clearly found that both films showed memory behavior, and so it could be used as nonvolatile ferroelectric random access memory. They satisfied the essential requirement for the development of MFIS. 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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