Tunable 소자 응용을 위한 Sol-gel 법으로 제작된 $(Pb_{0.5},Sr_{0.5})TiO_3$ 박막의 stain 과 유전 관계

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Correction between Dielectric and Strain in PST Thin Films prepared by Sol-gel method for Tunable application

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Abstract

Pb0.5Sr0.5TiO3 (PST) thin films were fabricated by the alkoxide-based sol-gel process using spin-coating method on Pt/Ti/SiO2 /Si substrate. The PST films annealed from 500C to 650C for 1h show a perovskite phase and dense microstructure with a smooth surface. The grain size and dielectric constant of PST films increases with the increase in annealing temperature, which reduces the SiO2 equivalent thickness of the PST film. The crystallinity or internal strain in the PST thin films analyzed from the diffraction-peak widths correlate well with the decrease in the dielectric losses. The dielectric constants and dielectric loss (%) of the PST films annealed at 650C (teq = 0.89 nm) were 549 and 0.21%, respectively.

Key Words : Dielectric properties; Sol-gel, Tunable,

1. 서 론

Ferroelectric materials are of great interest for the application in ferroelectric and paraelectric thin film capacitors for dynamic random access memory (DRAM) devices and nonvolatile memories [1]. $PbLaTiO_3$ (PLT) [2], SrTiO3 [3], and (Ba,Sr)TiO3 (BST) [4] films have been intensively investigated due to theirhigh dielectric constant and good thermal stability. BST films have been regarded to be the most promising dielectrics of future high-density gigabit DRAM application. The reason is that BST films have several advantages, such as a low leakage current, room-temperature paraelectric properties with an approximate ratio of Ba/Sr, and a high dielectric breakdown. However, high processing temperature (above 650°C) and low onset fieldfor high current emission (300-500 kV/cm)have restricted the application of BST thin films in DRAM devices [5].

B. Dibenedetto et al. investigated polycrystalline samples in the (PbxSr1-x)TiO3 (PST) ceramic system and established a complete series of solid solution from PbTiO3 (PTO) (Tc = 485°C, Tc Curie temperature) to

SrTiO3 (STO) (Tc = - 237°C) [6]. By partially substituting Pb^{+2} ion site for Sr^{+2} ion site in $SrTiO_3$, one can set the lattice constant and Curie temperature over a wide range. The STO films have a cubic phase at room temperature while the crystallization temperature is lower compared with BST films. On the other hand,the dielectric constant is also lower than that of BST films. Tetragonal PTO films show higher dielectric constant than STO films at room temperature. H. J. Chung proposed that the addition of lead oxide into STO would not only enhance the dielectric constant but also reduce the deposition temperature [7]. (Pb0.5Sr0.5)TiO3 films have a Curie temperature below room temperature, resulting in a paraelectric properties with a high dielectric constant. Therefore, it is possible to use in DRAM application due to their high dielectric constant and low crystallization temperature.

Many techniques have been successfully applied to the deposition of high quality dielectric thin films including dry methods such as sputtering, laser ablation, and chemical vapor deposition (CVD), as well as chemical methods such as sol-gel, and metal-organic decomposition (MOD) [8-11]. Among many deposition methods, the sol-gel method, in general, is characterized by the their simplicity, lower cost, easy compositional control in thin films with high quality and microchemical homogeneity. However, there have been only few papers that deal with the dielectric properties of PST thin films for DRAM applications.

In this study, dielectric (Pb0.5Sr0.5)TiO3 thin films were fabricated by a sol-gel method. The PST films were spincoated onto the Pt/Ti/SiO2/Si substrate. We investigated the correlation of internal strain and dielectric properties with annealing temperature.

2. 실 험

(Pb0.5Sr0.5)TiO3 precursor solutions were prepared by sol-gel method from lead acetate trihydrate [Pb(CH3CO2)33H2O], strontium acetate hydrate [Sr (CH3CO2)XH2O], and titanium iso-propoxide {Ti[OCH(CH3)2]4} as starting materials. Acetic acid [CH3CO2H] and 2-methoxyethanol [CH3OCH2CH2OH] were used as solvents. A 10% excess amount of lead acetate was used to compensate the Pb-loss during annealing process.Then, clear solutions were added to the solution of titanium iso-propoxide in 2- methoxyethanol to prepare a stoichometric, clear, and stable PST precursor. The concentration of PST stock solution was adjusted to 0.25M under a flowing nitrogen atmosphere. The ethylene glycol(three moles of ethylene glycol per one mole of 2-methoxyethol) was added to the stock solution under agitation to adjust viscosity, and surface tension of the precursor. The ethylene glycol stabilized the solution to prevent precipitation, and it was also found that the BST solution precipitated after only several hours without ethylene glycol [12]. The solution was clear and transparent. For the fabrication of PST thin films, the stock solution were syringed through a 0.2 m syringe filter on the Pt(120 nm)/Ti(30 nm)/SiO2/Si substrate. Wet films were deposited by spinning the coating sol onto Pt substrate at 4000 rpm for 30 s. This coating/drying circles was repeated up to 8 times. After spin-coating on to Pt, films were kept on a hot plate at 400C in air for 10 min to remove the organic materials. The pre-baked films were annealed at various temperatures 500 ~ 650C for 1 h under an oxygen atmosphere for crystallization. The final thickness of the PST film was about 160 nm. The dielectric measurements were carried out in the metal-insulator-metal (MIM) capacitor structure. For electrical measurements, top electrodes with 200 m diameter were fabricated by depositing a 150-nm-thick Pt film at room temperature using dc magnetron sputtering. X-ray diffraction (XRD) profiles were obtained using CuK radiation source at 30 kV and 60 mA (Rigaku-D/MAX) to determine the crystallinity of the PST thin films.

The surface and cross-sectional microstructures were examined using a JEOL 6330F field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM, Digital Instrument' NanoScope IIIa). The capacitance-voltage characteristics, dielectric constant, and dielectricloss were measured using an HP 4192 impedance analyzer. The leakage current densities of PST thin films were measured using a HP 4145B semiconductor parameter analyzer at conditions of 0.1-V step voltage and delay time of 1s.

3. 결과 및 고찰

Figure 1 shows the XRD patterns of the PST thin films corresponding to various annealing temperatures. All films showed a nontextured polycrystallinestructure with no evidence of secondary phases formation. The XRD pattern of the PST film annealed at 500°C shows polycrystalline structure that revealed by the presenceof such peaks as (100), (110), (111) and (211). This fact indicates that the onset of crystallization into the perovskite phase is close to 500°C. Therefore, we inferred that the annealing temperature of PST thin films is lower than that of BST thin film. However, as the annealing temperature increased, the peak in the XRD pattern became sharper, indicating that the structure of PST was better at high annealing temperature. The peak intensities of the PST films increased and the full widths at half maximum (FWHM) of the PST films decreased during the increasing annealing temperature presumably because the grain size was increasing resulting in less internal strain.

To qualitatively estimate internal strain of PST thin films, the full width at half maximum (k) of XRD peaks were fitted for each peak with the scattering vector k =(4/)sin, using a double Lorentzian function. It is known that a simple expression of internal strain can be used to describe k vs k:

$$k = 2/D + (d/d)k, \quad (1)$$

where D is the effective grain size suggested by Scherrer, and d/d is the internal strain derived from the Bragg relation [14]. The dependence of internal strain on annealing temperature is shown in Fig. 2 for PST thin films. The internal strain of PST thin films decreased with increasing annealing temperature. We can assume that the internal strain in the film, such as nonuniform distribution of local strain, is caused probably by non-stoichiometry, point defects, dislocations and stacking faults, etc.

The relative dielectric constant, dielectric loss and equivalent oxide thickness (teq) of PST thin films with different annealing temperature are listed in Table 1. Dielectric constant and dielectric loss of the films was measured at 100 kHz and an oscillation voltage of 0.1 V. The dielectric constant gradually increased and dielectric loss decreasing with increasing annealingtemperature. In our opinion, the change in dielectric constant may be related to the variation of the grain size and crystallinity. The dielectric loss is dependent on annealing temperature. The decrease in internal strain in the PST thin films corresponds very well to the reduction of dielectric loss, as shown in Fig. 3. Lower crystalline structure in films represented by internal strain cause anharmonic lattice motion, leading to high dielectric loss. The dielectric constants and dielectric loss (%) of the PST thin films annealed at 650°C were 549 and 0.212%, respectively. As a result, the PST thin films annealed at the temperature of 650°C show highest dielectric constant and lowest equivalent oxide thickness. Generally, increase of dielectric constant may be connected with two factors such as improvement of crystalline structure of PST thin films and variations of grain size. First factor is partially confirmed by the data of Fig. 2 discussed above. However, the data of Fig. 1 do not show the noticeable improvement of

crystalline structure as the annealing temperature increases from 550°C to 650°C. At the same time, dielectric constant increases from 370 (550°C) to 549 (650°C).

4. 결 론

In this work, we reported correlation between dielectric properties and internal strain in PST thin films. The XRD analysis shows that all films possessed a nontextured polycrystalline structure with no evidence of secondary phase formation. AFM shows that the RMS surface roughness and average grain size of the PST thin films increase with increasing annealing temperature. As the annealing temperature increased, the dielectric constant increased and dielectric loss decreased. The crystallinity or internal strain in the PST thin films was analyzed from the diffraction-peak widths, and correlated well with the decrease in the dielectric losses. The dielectric constants and dielectric loss ofthe PST thin films annealed at 650°C (teq = 0.89 nm) were 549 and 0.21%, respectively.

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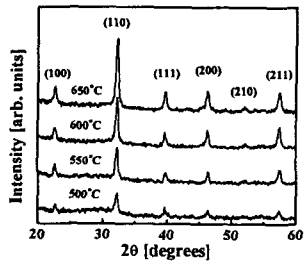

Figure 1. X-ray diffraction patterns of PST thin films for various annealing temperatures.

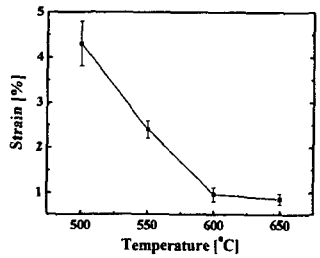

Figure 2.The estimated strain from the x-ray diffraction peak widths various angles of PST thin films at different thickness using Eq. (1).

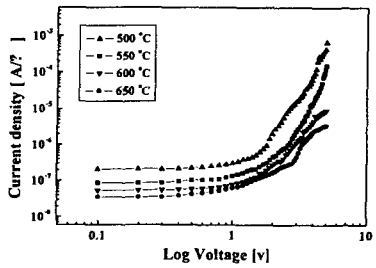

Figure 3. Leakage current density of PST thin films as a function of annealing temperature.

Table 1. The relative dielectric constant, dielectric loss and equivalent oxide thickness (teq) of PST thin films with annealing temperature.

Annealing temperature (°C)	500	550	600	650
Dielectric constant	254	370	419	549