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Electrical Characteristics and Preparation of $(Ba_{0.5}Sr_{0.5})TiO_3$ Ferroelectric Films by Spray Pyrolysis and Rapid Thermal Annealing

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Abstract —Ferroelectric films of $(Ba_{0.5}Sr_{0.5})TiO_3$ on $Pt/Ti/SiO_2/Si$ substrates are prepared by spray pyrolysis and rapid thermal annealing. Barium nitrate, strontium nitrate and titanium isopropoxide are used as starting materials, while ethylene glycol thus is used as solvent. For ferroelectric thin film, thermal characteristics of the precursor powder which scratch from as-sprayed films show a remarkable peak at around 300-400°C and 57.7% weight loss up to 1000°C. The as-sprayed precursor film with coffee-like color and amorphous-like phase transform into the resultant film with white, crystalline perovskite phase with characteristic peaks (110) and (100). The resultant films show dielectric constant, leakage current and dissipation factor of the resultant films increase with increasing annealing temperature.

Keywords —Ferroelectric film, barium-strontium-titanate, spray pyrolysis, leakage current, dielectric constant

1 Introduction

Barium strontium-titanate with perovskite structure has been resulted in a considerable attention due to potential applications microelectronic devices. Physical properties of $[(Ba,Sr)TiO_3,BST]$ include large dielectric constant, large spontaneous polarization and so on. Specially, it is suitable for applications in DRAMs and NVRAMs[1)].

Nowdays, preparing high-quality BST films adopted various techniques. These techniques include physical vapor deposition such as rf-sputtering, molecular beam epitaxy, laser ablation and chemical vapor deposition of metalorganic deposition, spray pyrolysis, sol-gel[2-3)] and so on. Especially spray pyrolysis[3)], this technique is a simplified and convenient process and has extensively used on the fabrication of oxide films and fining powders with nanometer size. Reviewing to previous literatures related to the fabrication and electrical characteristics of BST thin films, there are not so many paper discussed this idea. This paper, we investigated the preparation and ferroelectric properties of single-phase BST films on Pt $/Ti/SiO_2/Si$ substrates via spray pyrolysis of organic solution.

2 Experiment Procedure

For the preparation of BST film, the precursor solution of barium nitrate, titanium isopropoxide, strontium nitrate are basic materials. The mixed solution of nitrates with solvents heated up to 120°C under stirring to eliminate water. Adhesion ability between Pt and SiO_2 is poor, so Ti layer is often deposited as a buffer layer and also functioned as a diffusion barrier for preventing the formation of Pt silicides.

The spin-on and spray pyrolysis applied to prepare ferroelectric BST films. Firstly, precursor solution is spin-coated on the Pt, Ti-coated thermal oxidized Si wafer. After spin-coating, dry them at 300°C for 30mins. Secondly, the as-sprayed films are formed on the Pt(1000A)/Ti(100A)/ SiO_2(2000A)/Si substrates with spin-coated precursor film by spraying the precursor solution using a spray gun and then once more heated at 300°C. Typical thickness of as-sprayed films is about 1.0μm. To find the optimal conditions for the preparation of ferroelectric film with high dielectric constant, as-sprayed films are rapid thermal annealed at temperatures of 550°C, 600°C, 650°C, 700°C and 750°C for 3mins.

The polarization versus electric field and hysteresis characteristics of the resultant films are observed by using a Sawyer-Tower circuit at 1 kHz. Relation of current-voltage of the resultant films are measured by HP-4145.

3 Results and Discussion

Thermal characteristics of BST precursor powder show two characteristic peaks in thermal measurement. The first sharp peak follows with a weight loss of 50.8% appeared at temperatures 300°C~400°C. This should be a reaction of residual nitrates and organic compounds and resulted in formation of oxide film. The second characteristic peak is found at temperature of 583.4°C. The small weight loss of 3.1% at temperatures below 236°C should be evaporation of moisture and solvent, while weight loss of 3.4% at around 580°C and 890°C may be due to formation of intermediate compounds, i.e. phase transformation.

Figure 1 shows XRD patterns of as-sprayed film(a) and also contains with BST resultant films which annealed at temperatures of 550°C(b), 600°C(c), 650°C(d), 700°C(e) and 750°C(f). The as-sprayed precursor film exhibits coffee-like color on surface and amorphous-like phase. When annealing temperature raised above 550°C, (110) and (100) peaks of BST films will gradually appear and relative intensities of characteristic peaks will increase with increasing annealing temperature. These characteristic peaks have detected and identified to be the cubic perovskite phase. Except that phase transformation of amorphous to crystalline cubic perovskite, color on surface of films also change from coffee-like to white. Annealing at higher temperature and longer duration result in occurrence of interface reaction between film and underlying film and the formation of second phase.

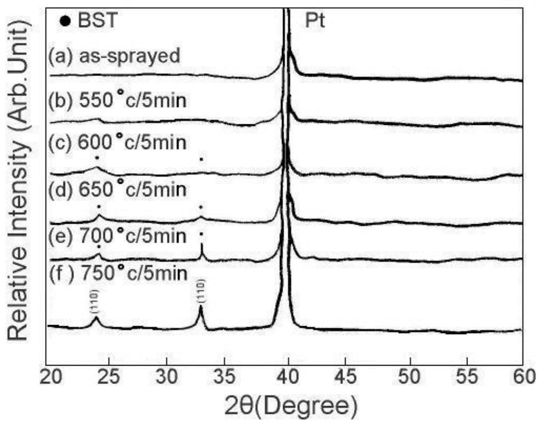

Figure 1 shows XRD patterns of as-sprayed(a) and BST films annealed at temperatures of 550°C(b), 600°C(c), 650°C(d), 700 °C(e) and 750°C(f) for 5 min.

The change of dielectric constant and dissipation factor depends on annealing temperature. Figure 2 presents this symptom, and resultant films are measured at 1 kHz and room temperature. The dielectric constant of resultant films increases with increasing annealing temperatures from 550°C to 750°C. When Sr is substituted for Ba to be a solid solution, dielectric constant will increase dramatically. It is demonstrated that an artificial superlattices of $SrTiO_3$/ $BaTiO_3$ films with a stacking periodicity shows higher dielectric constant than BST films with change of temperature. The tangent loss inferred to result from the leakage current through the loss by a parallel resistance. Therefore, the increase of tangent loss related to leakage current and resistance. It indicated dissipation factor of films increase with increasing annealing temperatures.

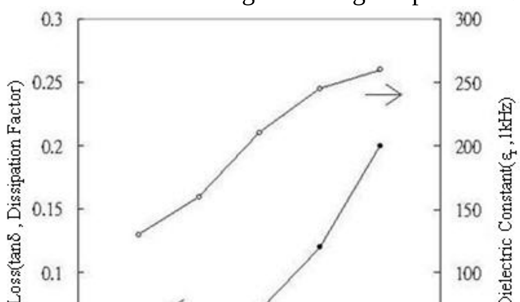

Figure 2 shows annealing temperature dependence of dielectric constant and dissipation factor for the resultant films.

Figure 3 shows the relationship between leakage current density of BST resultant films at 50kV/cm^2 and annealing temperatures. The leakage current density of the resultant films will increase if annealing temperature raise. That is because when annealing temperature changed, grain size and structure will also be changed which affected the leakage current density. If annealing temperature is higher than 600°C, the columnar structure will be formed whose leakage current density is larger, if annealing temperature is lower than 600°C, granular structure will be formed whose leakage current density is lowered.

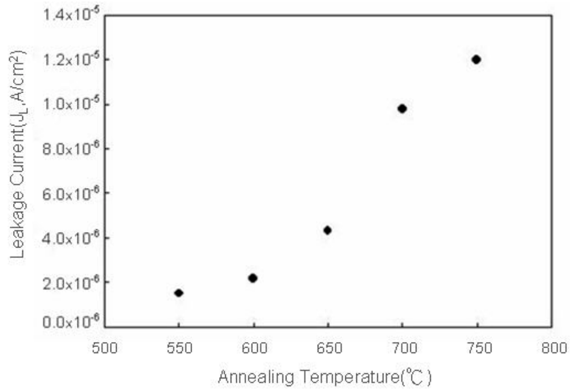

Figure 3 shows relationship between leakage current density of BST films at applied field 50kV/cm^2 and annealing temperatures.

Typical current-voltage curve of BST films is shown on Figure 4, and BST films are annealed at temperatures of 650°C(a) and 750°C(b) for 5mins. The leakage current density of BST films annealed at 650°C is 4.5x10^{-6}A/cm^2 at 50kV/cm, which is lower than the resultant film annealed at 750°C. The higher leakage current density when ferroelectric films annealed at higher temperatures may be due to formation of oxygen vacancies in the interfaces.

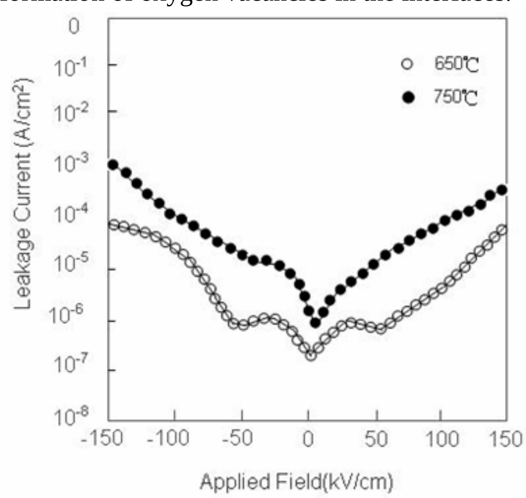

Figure 4 shows typical current-voltage curves of ferroelectric BST films annealed at temperatures of 650°C(a) and 750°C(b) for 5min.

4 Conclusion

Ferroelectric film of BST have been prepared by spray pyrolysis and rapid thermal annealing on substrate of Pt- and Ti-coated on silicon with a thin layer of thermal SiO_2. The dielectric constant, leakage current and dissipation factor of the BST resultant films increase with increasing annealing temperatures. The dielectric constant is 264 and a tangent loss is 0.21 in the resultant films annealed at 750°C for 5mins while leakage current density is 1.5x10^{-6}A/cm^2 in the film annealed at 550°C for 5mins.

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