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To cite this article: Hyun Jin Chung , Jin Hong Kim , Won Seok Moon , Seung Bin Park , Cheol Seong Hwang , Moon Yong Lee & Seong Ihl Woo (1996) Preparation of BST thin films on Pt electrode on Si wafer with down-flow LSMCVD reactor, Integrated Ferroelectrics, 12:2-4, 185-197, DOI: [10.1080/10584589608013062](https://doi.org/10.1080/10584589608013062)

To link to this article: <http://dx.doi.org/10.1080/10584589608013062>



Published online: 19 Aug 2006.



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PREPARATION OF BST THIN FILMS ON Pt ELECTRODE ON Si WAFER WITH DOWN-FLOW LSMCVD REACTOR

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(Received 27 May 1996)

A novel type of down-flow LSMCVD (Liquid Source Mist CVD) reactor was developed to prepare a high dielectric BST thin film on Pt electrode on Si wafer. Barium acetate [Ba(OOCCH₃)₂], strontium acetate [Sr(OOCCH₃)₂], and titanium isopropoxide [Ti(OC₃H₇)₄] were used as metal sources. Metal sources were dissolved in acetic acid, 1-butanol, or 2-methoxyethanol. BST [Ba/(Ba + Sr) = 0.7] film annealed on Pt/Ti/SiO₂/Si above 650°C was polycrystalline. BST film has a (110) preferred orientation with increasing temperature. Surface roughness of BST film and grain size increased with increasing temperature. The metal-oxygen bond was formed at 650°C as shown in the spectra of FTIR. The depth profiles of elements of BST thin films indicated a uniform composition throughout the film. BST films annealed at 750°C showed a dielectric constant and a tanδ of 390 (thickness: 150 nm) and 0.06 at a frequency of 100 kHz, respectively. The behavior of capacitance of the BST film with bias voltage showed paraelectric property. BST film annealed at 750°C had the leakage current density of 3.2 (μA/cm²) at a bias voltage of 2V.

Keywords: BST; ferroelectric; LSMCVD; DRAM capacitor

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INTRODUCTION

As integration of memory cell is increased, conventional $\text{SiO}_2/\text{Si}_3\text{N}_4$ structure can not be used as a capacitor for ULSI DRAM. To solve this problem, many perovskite thin films have been extensively investigated because of their interesting dielectric properties. $\text{BaTiO}_3(\text{BT})$,^[1] $\text{SrTiO}_3(\text{ST})$, $(\text{Ba}, \text{Sr})\text{TiO}_3(\text{BST})$ and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3(\text{PZT})$ ^[2] have been proper candidates. Recently, the most promising material for the capacitor of ULSI DRAM cell was $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3(\text{BST})$.^[3-5] BST with high dielectric constant and paraelectricity at general operating temperature have attracted great attention for a practical use in capacitor for ULSI DRAMs.

The dielectric constant of BST varied with the Ba/Sr ratio. Furthermore, BST near $x=0.7$ shows the maximum dielectric constant of above 10000 at room temperature. Accordingly, in order to obtain the desired dielectric constant, control of the film composition is important. And compatibility to another process, reproducibility of film properties on large area, and uniformity of film thickness are required for fabrication of application devices, too. Especially, the tendency to integrate silicon integrated circuits creates the need for a technique capable of growing high dielectric oxide thin films on large pre processed Si wafers. Sputtering,^[6] chemical vapor deposition (CVD),^[7-8] sol-gel,^[9] LSMCVD,^[10] and laser ablation^[11-12] methods were evaluated for ferroelectric thin films. BST thin film have been prepared by these methods, too.

Among these methods, LSMCVD in which proper organic solvents with metalorganic precursor was converted to fine mist by ultrasonic nebulizer have been scarcely reported in spite of its potential advantages such as high deposition rate, ease of controlling composition, uniformity in a large area, and easy processing (room temperature and low vacuum deposition), which may be due to the complexity of the mist movement and the difficulty of preparation of precursor solution.

In this study, BST thin films were prepared by the LSMCVD method using Barium acetate $[\text{Ba}(\text{OOCCH}_3)_2]$, strontium acetate $[\text{Sr}(\text{OOCCH}_3)_2]$ and titanium isopropoxide $[\text{Ti}(\text{OC}_3\text{H}_7)_4]$ in organic solvents such as acetic acid, 1-butanol, 2-methoxyethanol and etc., and their structures, chemical changes, and dielectric properties were investigated.

EXPERIMENTAL DETAILS

A ultrasonic nebulizer (HU-350, Samsung Electronic Co., Ltd. Frequency of sonicator: 1.63 MHz) was used to make mist of precursor solution. In order

to prevent sonicator damaging by corrosion or precipitation of precursors which were composed of metal alkoxides and metal salt, precursor solutions were put in a glass flask. The temperature of solution was remained uniformly while making mist. The mist was transported to main chamber by carrier gas (N_2). At the same time, the pressure in chamber was remained constant by pumping. Figure 1 shows the flow diagram for the formation of BST thin films by LSMCVD.

After Ba acetate and Sr acetate were mixed in acetic acid, it was possible to make a mist after diluting it with 2-methoxyethanol, 1-butanol or benzene. And then titanium isopropoxide was dissolved stoichiometrically, P-type Si(100) and Pt(100 nm)/Ti(20 nm)/SiO₂(100 nm)/Si were used as substrates. They were deposited with mixed solution to form homogeneous precursor films and dried at 120°C for 5 min in air. The films were subsequently heated at 300°C for 5 min in air. The thickness of the films was controlled by repeating deposition and pyrolysis process. Furthermore, post-deposition annealing of LSMCVD BST thin films was performed using a

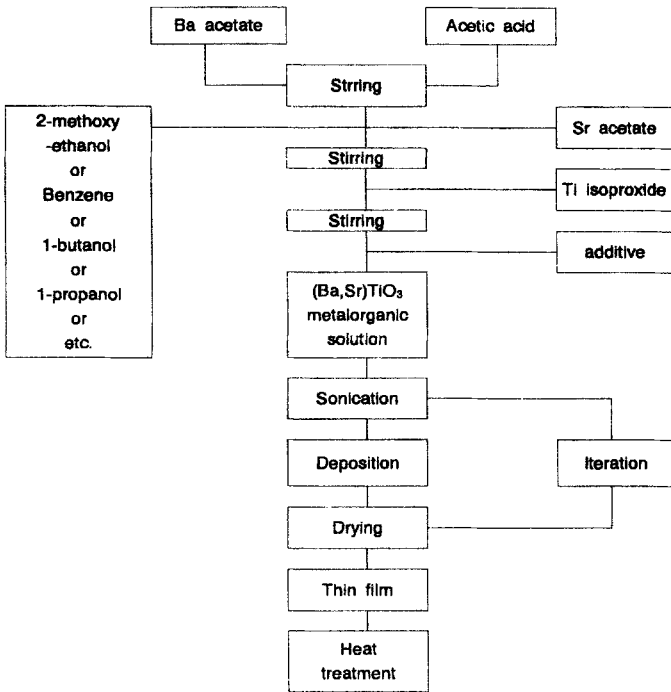


FIGURE 1 Flow diagram for formation of BST thin films by LSMCVD.

horizontal furnace in the range of temperature between 600 and 750°C under O₂ ambient for 1 hr. The heating rate of temperature was fixed at 10°C/min. The detailed growth conditions of BST thin films are shown in Table I.

Thermogravimetry and differential thermal analysis (TG-DTA, Dupont 950-DTA, 951-TGA) measurements for the precursor (dried at 60°C for 12 hr) were carried out to estimate drying and pyrolysis temperatures. The thickness and refractive index were measured optically by using ellipsometer (Rudolph research ellipsometer mode auto EL-III). The surface morphology of thin films were analyzed with scanning electron microscope (SEM, Philips 533M). Particularly, the cross-sectional SEM photographs were compared with the results of ellipsometer to make no errors in measuring thickness. The extent of crystallization and the direction of crystallites were measured by X-ray diffractometer (Rigaku, D-MAX-RC, Cu target, Ni filter). The composition of thin film was analyzed by using wavelength dispersive spectroscopy (WDS, Microspec 3-PC). And the depth profile was obtained by using Auger electron spectroscopy (AES, Perkin-Elmer PHI 610). The chemical structures were analyzed with FT-IR (Bomem-102). In order to measure electrical properties, metal-insulator-metal (MIM) structure with Pt electrodes was fabricated. Pt upper electrodes of 0.3 mm diameter was prepared by using shadow mask in the dc-magnetron sputter. (Capacitance-Voltage (C-V) characteristics were measured by using impedance analyzer (HP4192A) at 100 kHz frequency. The dielectric constant was calculated by using the measured capacitance and film thickness. The leakage current (I-V) characteristics were measured with picoampere current meter (HP4145B) with the conditions of 0.05 V of step voltage and 1 sec of delay time.

TABLE I The growth conditions of BST thin film by LSMCVD

Liquid Source Temperature	R.T – 50°C
Pressure during Deposition	200–600 mmHg
Frequency of ultrasonicator	1.63 MHz
Substrate Temperature	Room temperature
Post-Deposition Baking	120–450°C
Post-Deposition Annealing	600–800°C
Typical Deposition rate	0–20 nm/min
N ₂ flow rate	300–1000 sccm
Substrate	bare Si(100) or Pt/Ti/SiO ₂ /Si
Rotating speed	0–300 rpm

RESULTS AND DISCUSSIONS

Figure 2 shows the results of TG-DTA of precursor powder. The weight decrease occurred from room temperature to about 200°C is caused by the evaporation of solvents. The small weight loss from 200°C to 300°C is due to the evaporation of residual solvents and additive. The large weight loss and large heat flow occurring from 300°C to 450°C are due to pyrolysis and combustion of organic components. The weight becomes almost constant above 450°C. Especially, this result shows the precursor solution decomposed rigorously at about 300°C. Based these results, drying temperature of 120°C and pyrolysis temperature of 300°C were chosen. In order to understand in detail the processes taking place during the formation of the films, the change of chemical bonding in BST thin films was monitored by FTIR during the decomposition process. Figure 3 shows the FTIR spectra of BST thin films heated at various temperatures. The spectrum labeled at 250°C exhibits absorption bands corresponding to carboxylate ion (1570 cm^{-1} and 1420 cm^{-1}) due to residual solvents such as acetic acid and

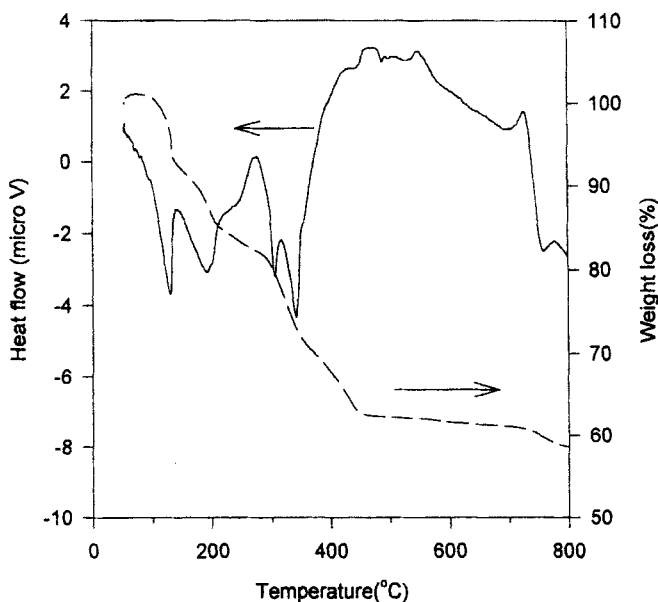


FIGURE 2 TG-DTA curve for the powder of precursor solution dried at 60°C for 12 hr mixed at the Ba: Sr: Ti molar ratio of 0.70: 0.30: 1.00.

2-methoxyethanol.^[18] In case of spectrum of 350°C, carboxylate peak was drastically decreased and the broader peak arising from C-H modes and carbonate appeared. From this result and the results of TG-DTA, it can be concluded that weight loss between 250 and 350°C resulted mainly from the evaporation of the solvents. These peaks became broader and gradually disappeared with increasing temperature. Upon heat treatment at 500–650°C, peak at about 1440 cm⁻¹ is clearly observed in the FTIR spectra. This band can be assigned to carbonate ions. The formation of carbonate ion was also reported by other researchers.^[19] Upon heat treatment at 700°C, the carbonate bond disappeared. Upon heat treatment above 650°C, Ti-O stretching band arising from either BST or TiO₂ was shown in Figure 3. This result suggests that the perovskite phase of BST was formed above 650°C. This result is consistent with that of XRD.

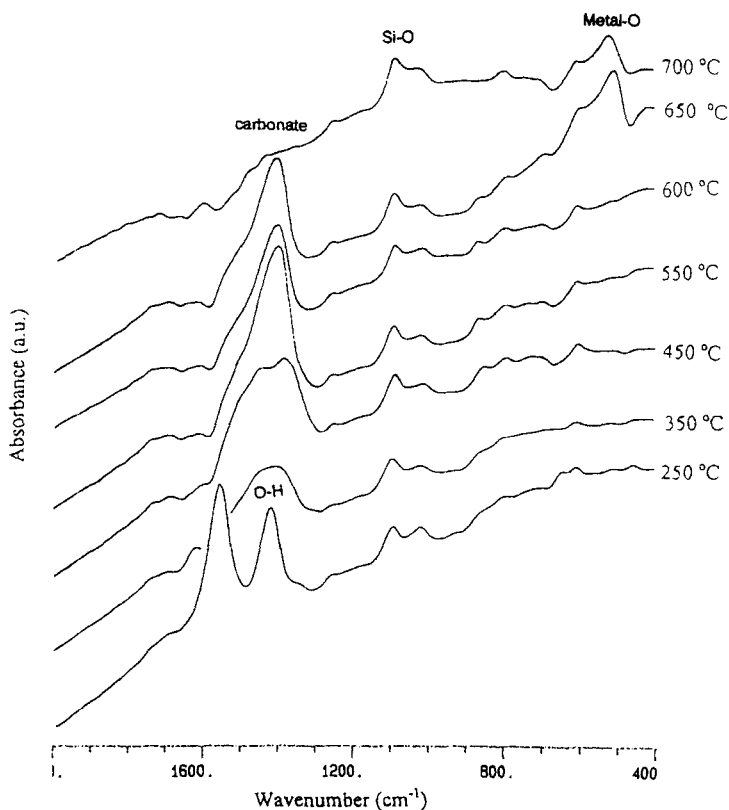


FIGURE 3 FTIR spectra of BST after heat treatment between 250 and 700°C.

The elemental composition of the deposited film and precursor solution at various annealing temperatures were obtained by using wavelength dispersive spectroscopy (WDS) as shown in Figure 4. Elemental compositions are not much different between film and precursor solution and the change in the composition was not occurred at various annealing temperatures. The elemental component distribution of LSMCVD (Ba,Sr)TiO₃ and the contaminants on the surface of BST thin film were obtained by using auger electron spectroscopy (AES) as shown in Figure 5. Figure 5(a) is the AES spectrum of as-received (without Ar⁺ sputtering) BST thin film. The individual element signals were located at 383eV for Ti (denoted by Ti1), 510eV for O (denoted by O1), 272eV for C (denoted by C1), 584eV for Ba (denoted by Ba3), and 1649eV for Sr (denoted by Sr1)^[20]. As-received thin films are

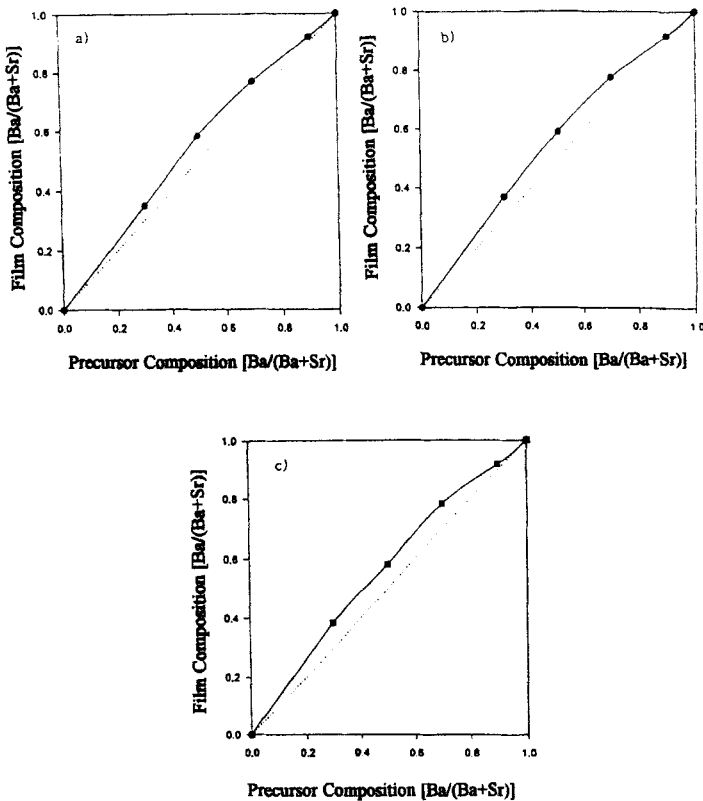


FIGURE 4 The elemental compositions of the deposited film and precursor solution measured by WDS. BST thin films were annealed for 1 hr on bare Si(100) at (a)450, (b) 650 and (c) 800°C.

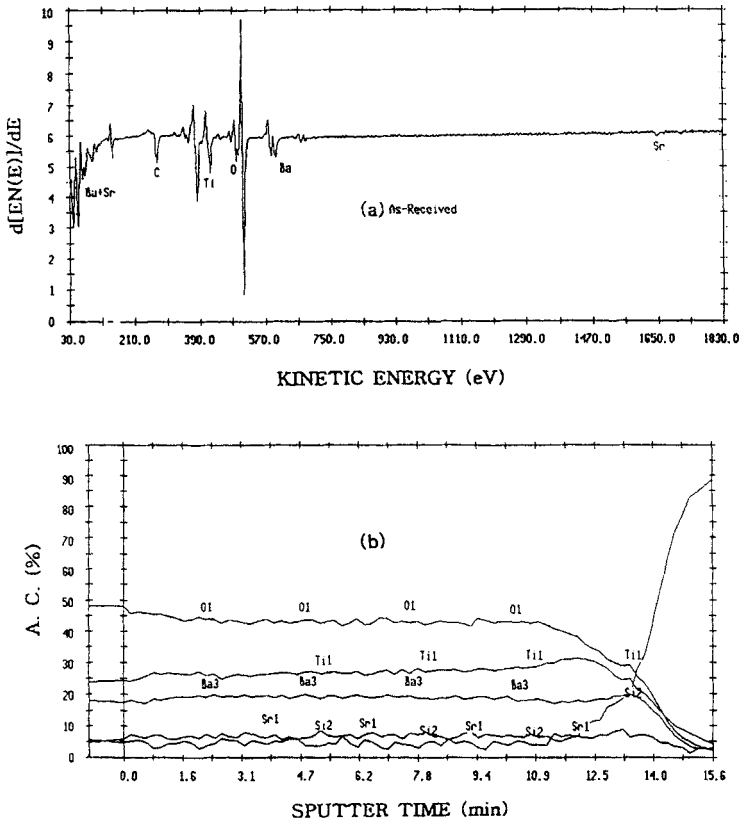


FIGURE 5 (a) AES spectrum (no Ar^+ sputtering) and (b) the depth profile of LSMCVD BST thin film annealed at 700°C on Si(100) measured by AES.

mainly composed of Ti, Ba, Sr, O, and C. After 0.2 min Ar^+ sputtering, the carbon disappeared. Carbon element is a major contaminant on the surface of BST thin film by LSMCVD. Similar results were reported in MOCVD or sol-gel due to the carbon originating from titanium isopropoxide.^[21] When TiCl_4 was used as a reactant for the PECVD for TiO_2 films, chlorine was identified as a major source of contamination^[22]. These contaminants should be eliminated in order to improve the electrical characteristics of BST thin film. Figure 5(b) is the depth profile of BST thin film. Each component shows a uniform distribution from surface to interface on substrate Si. The composition of BST thin films by LSMCVD was not changed much by heat treatment. BST is more stable at high annealing temperature than PZT and PbTiO_3 . Sputtering, MOCVD, and laser ablation methods showed some problems in stoichiometry control and

reproducibility. However, LSMCVD showed an excellent reproducibility of the film composition and easy control of the composition.

After deposition and pyrolysis were repeated twice, the thickness of the resultant film was 150 nm. The XRD patterns of the films heated in O₂ atmosphere at 650, 700, 750°C are shown in Figure 6. The perovskite phase of BST was obtained above 650°C. (110) peak became dominant as the annealing temperature was increased. Figure 7 shows the surface morphologies of the films heated at 450, 650, 750, and 800°C for 1 hr in a conventional furnace. In case of the film annealed at 450°C, amorphous phase was shown. The grain was formed above 650°C. The grain size increased to about 150 nm with raising temperature. The surface morphology was influenced also by the mist radius and solution concentration^[23]. The film

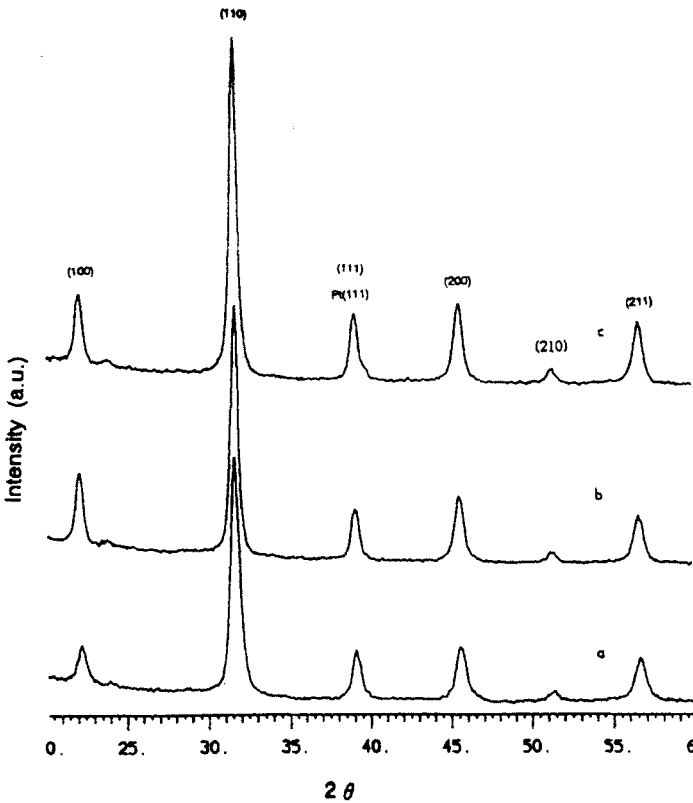


FIGURE 6 XRD patterns of BST thin films annealed in O₂ atmosphere at (a) 650, (b) 700 and (c) 750°C for 1 hr.

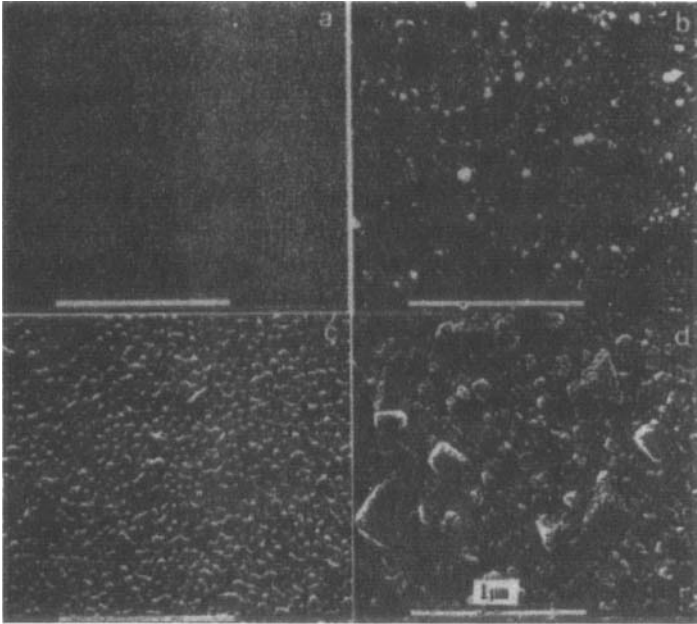


FIGURE 7 Surface morphology of the BST thin films annealed in O_2 atmosphere at (a) 450, (b) 650, (c) 750 and (d) 800°C for 1 hr.

showed polycrystalline phases, and the crystallization of grains on the surface at high temperature was complete. As annealing temperature was increased, the surface morphology became rougher. The uniform grains obtained after annealing the film at 750°C.

The capacitance-voltage (at 100 kHz) of the BST film annealed at 750°C for 1 hr is shown in Figure 8. It was confirmed that the perfect paraelectricity arising from the cubic phase was obtained in the BST film. Dielectric constant and $\tan \delta$ of the film were 390 and 0.06, respectively. They were similar in magnitude compared with other values reported previously.^[14–17] To achieve a high dielectric constant and a low $\tan \delta$ of the films in this study, oxygen defect contents and impurities in BST film should be minimized. The poor electric behaviors of thin films may be attributed to the existence of amorphous phase or empty phase between the grain boundaries. Therefore, the densification of BST film should be achieved by optimal heat treatment, changing metal precursor, and controlling concentration of precursor solution. It was reported that denser films increased the electron transfer between Ti and O.^[24] These enhanced Ti—O dipoles explain the increase in the total polarization in unit volume, resulting in the increase in

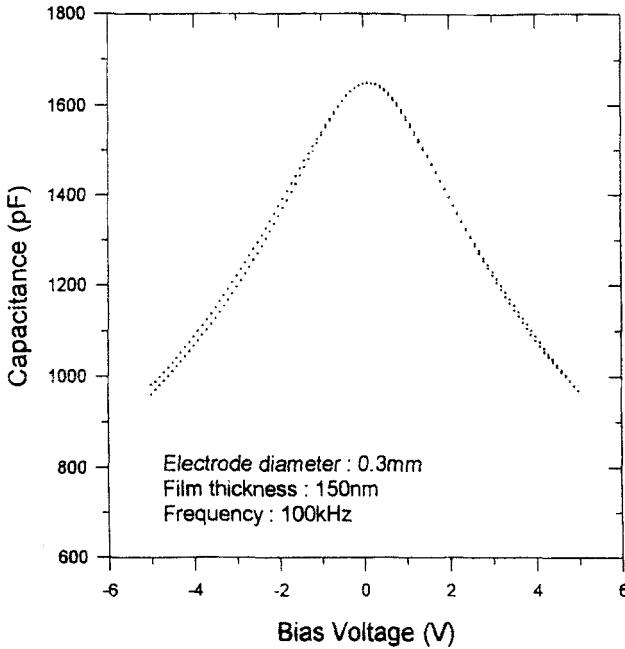


FIGURE 8 Capacitance-voltage characteristics of the BST thin film annealed on Pt/Ti/Si O₂/Si at 750°C for 1 hr in O₂ atmosphere.

the dielectric constant. Figure 9 shows the leakage current density of the BST film annealed at 750°C for 1 hr. When top electrode was biased positively, it was 3.2×10^{-6} (A/cm²). When top electrode was biased negatively, it was 3.3×10^{-5} (A/cm²) which was 10 times higher than that of the former. It can be explained as follows: Firstly, leakage current density depends on the distribution of defect which is able to work as a conductive part.^[1,2] Secondly, the reaction extent of electrode with film or the degree of diffusion of metal⁺ ions is dissimilar between the interfaces of film-electrodes because the thermal history of top and bottom electrodes is different.

SUMMARY

(Ba_{0.7}, Sr_{0.3})TiO₃ thin films having the uniform distribution of Ba, Sr, Ti and O elements throughout the bulk of the film were successfully prepared by liquid source mist chemical vapor deposition (LSMCVD). The LSMCVD BST thin films after annealing above 650°C under O₂ atmosphere for 1 hr were converted from an amorphous to a perovskite crystalline

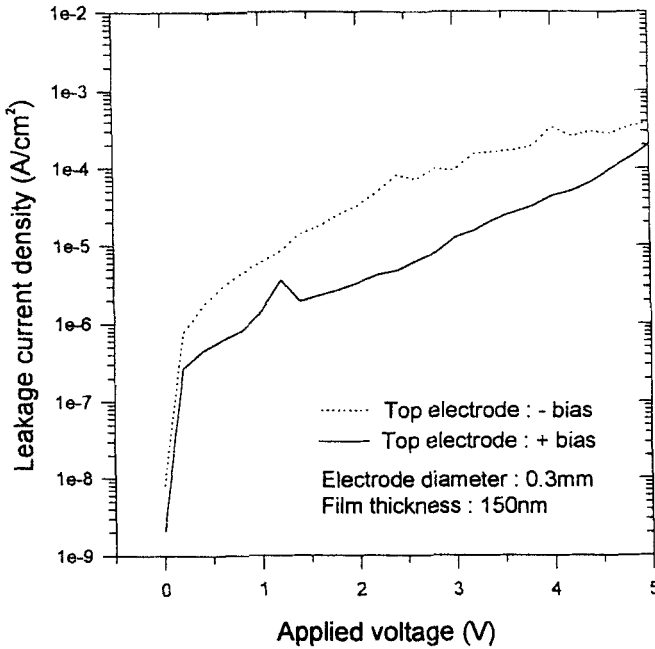


FIGURE 9 Leakage current density of the BST thin film annealed on Pt/Ti/SiO₂/Si at 750°C for 1 hr in O₂ atmosphere.

phase with preferred orientation of (110). Dielectric constant and $\tan \delta$ of the film were 390 and 0.06, respectively. The perfect paraelectricity was shown at room temperature. The leakage current density was 3.2×10^{-6} (A/cm²) at 2 V.

Acknowledgement

The authors thank Samsung Electronics Co., LTD for the financial support.

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