Influence of the Precursor Solutions on the Properties of BST Thin Films

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Abstract—We have studied the effects of solvents and additives in the precursor solutions on the characteristics of barium strontium titanate (BST) thin films. The solution having two solvents, ie. acetic acid for barium acetate and strontium acetate and 2-methoxyethanol for titanium isopropoxide and also having an additive of ethylene glycol shows good stability and remains homogeneous even after a month of ageing. It produces excellent BST thin film without cracks. Dielectric constant, loss tangent at 10kHz and leakage current density at 3V of the BST (70/30) thin film made from this solution are 339, 0.052 and 13.3μA/cm^2, respectively.

Index Terms—sol-gel, BST thin film, dielectric constant, leakage current

I. INTRODUCTION

As the density of memory cells increases for the next generation of DRAMs, the available area per cell decreases significantly. Hence for the capacitor dielectrics of future DRAMs, a critical need is growing large for new materials with high dielectric permittivities, high dielectric strengths, and low leakage currents [1].

Ferroelectric materials are well recognized to be promising capacitor dielectric materials for the DRAM application [2]. Among the ferroelectric materials, $Ba_{1-x}Sr_xTiO_3$ (BST) thin film is promising candidate material for ULSI DRAMs due to its paraelectric phase (for $x < 0.7$) at room temperature and thus no aging and fatigue effects [3]. BST thin films have been studied by many researchers using various thin film deposition techniques such as sputtering [4], laser ablation [5], CVD [6], and the sol-gel [7] method. Among the techniques, the sol-gel method has the great advantage of the precise composition control and the cost performance. The sol-gel method has also evolved the advanced conformal deposition method such as the mist spray method [8]. Despite of such advantages, the reports on the sol-gel formation of BST thin films are rarely found. This may be due to the difficulties in selecting the solvents and additives for the precursor solutions. Therefore, in this study, we have Studied the effects of solvents and an additive of precursor solutions on the quality of BST thin films.

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II. EXPERIMENTAL

Barium acetate ($Ba(CH_3CO_2)_2$), strontium acetate ($Sr(CH_3CO_2)_2$) and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) were used as starting materials. Acetic acid (CH_3COOH) and 2-methoxyethanol (2-MOE, $CH_3OCH_2CH_2OH$) were used as solvents and ethylene glycol ($C_2H_6O_2$) was used as an additive to stabilize the solution. Barium acetate and strontium acetate were dissolved upon heating in acetic acid. After the dehydrated solution of Ba-Sr was made, three different types of Ba-Sr-Ti coating solutions were prepared by adding one of the two different Ti solutions or an additive (TABLE I).

TABLE I Solvents and Additives for the Different Types of Solutions.

	Solution A	Solution B	Solution C
Solvent of Ba, Sr acetate	Acetic acid	Acetic acid	Acetic acid
Solvent of Ti isopropoxide	Acetic acid	2-MOE	2-MOE
Additive	×	×	Ethylene glycol

For solution A, acetic acid was also used as the solvent of titanium isopropoxide and no additive was added. For solution B, 2-methoxyethanol was used as the solvent of titanium isopropoxide and no additive was added. Solution C was the same as solution B except having an additive of ethylene glycol. Each solution was diluted with the previously mentioned solvents and additive. The composition and concentration of the obtained solutions were $Ba_{0.7}$-$Sr_{0.3}$-Ti and 0.5M, respectively. Through this procedure, very clear and homogeneous solutions were consistently obtained.

The solutions were filtered by 0.2μm filters and spin-cast onto the Pt(1000 Å)/Ta(200 Å)/SiO_2(1000 Å)/(100)Si wafers by using the spinner at 7500rpm for 90 sec. within the clean bench. Thin films (0.40μm thick) were fabricated by multiple depositions accompanied by drying at 300℃ for 10min. between layers, and for 15min. after the last layer. Crystallization of the dense amorphous layers was performed at 750℃ for 30min. in air. The heating procedure was carried out in a conventional tube furnace and designed on the basis of on TGA and DTA characteristics for the BST gels dried at 80℃.

Ag top electrodes of 0.4mm in diameter, were thermally evaporated through a shadow mask placed on top of the wafers. The monolithic Ag-BST-Pt capacitors were completed by obtaining back-contact through acid-etching portions of the films. Crystal phase and microstructure of the thin films were determined by low angle X-ray diffraction using CuKα radiation (Philips,) and scanning electron microscopy (Hitachi, S-4200). Low-electric field measurements were carried out on an LCR meter (Standford Research, SR 720). The leakage current (I-V) characteristics were measured on a Semiconductor Parameter Analyser (HP 4145B).

III. RESULTS AND DISCUSSION

The three types of solutions were aged for longer than a month at room temperature. The result showed that the ageing of a couple of days caused white precipitates in solution A whereas solution B and solution C were remained homogeneous even after a month.

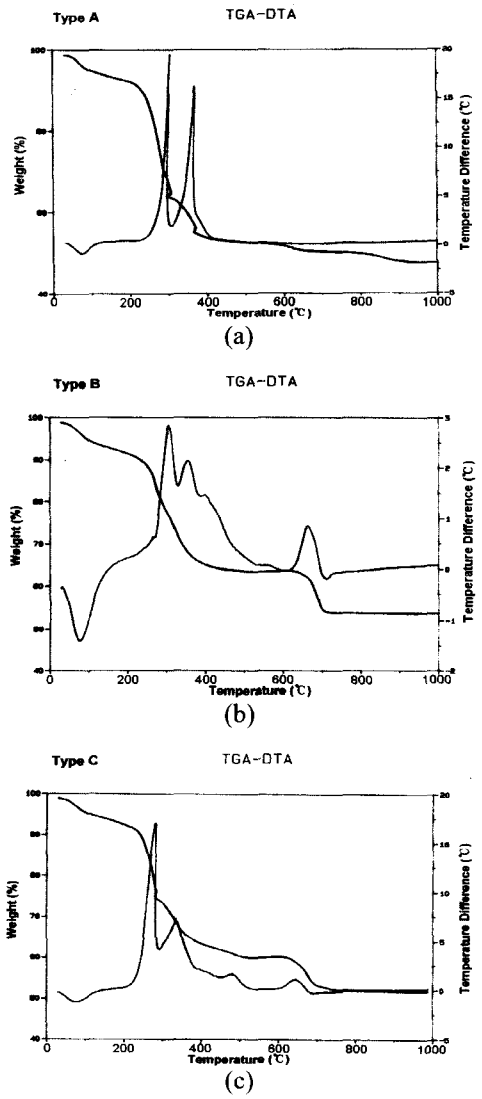

Fig. 1 TGA-DTA curves of (a) BST gels A, (b) B and (c) C heat-treated at 80℃.

Thermal decomposition behavior of the BST dried gels obtained from each solution are shown in Fig. 1 For all of three types of gels, the endothermic peak on the DTA curve and the weight loss on the TGA curve at near 100℃ are due to vaporization of the solvent, and the large exothermic peak and the large weight loss at 300~400℃ are due to the vaporization of residual organics. For the gels B and C, the exothermic peak at 650℃ is due to the formation of crystalline phase. Interestingly, however, such a peak at 650℃ is hardly found for the gel A.

Surface conditions of the BST thin films made from the each solution were observed by using the optical microscope at the magnification of 200 and are shown in Fig. 2. The surface micrographs of the BST film made from solution B and solution C (BST films B and C) show excellent surface conditions without cracks whereas that of the BST film A shows severe cracks.

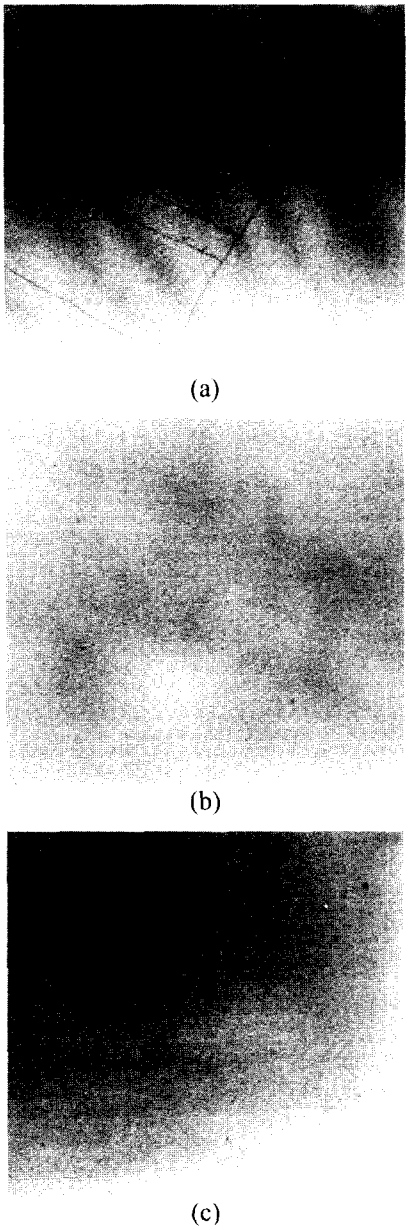

Fig. 2 Optical photographs of (a) BST thin films A, (b) B and (c) C.

Low angle X-ray diffraction (XRD) patterns of the BST thin films made from each solution are shown in Fig. 3. All of the peaks are identified as coming from the perovskite phase for all of the three BST thin films. However, the peak intensities for the three BST thin films are different even though the XRD measurements were performed in the exactly same conditions. The peak intensity from the BST thin film A is the smaller than those from the films B and C. From this, it can be deduced that the crystallinity of the film A is the worst among the three films.

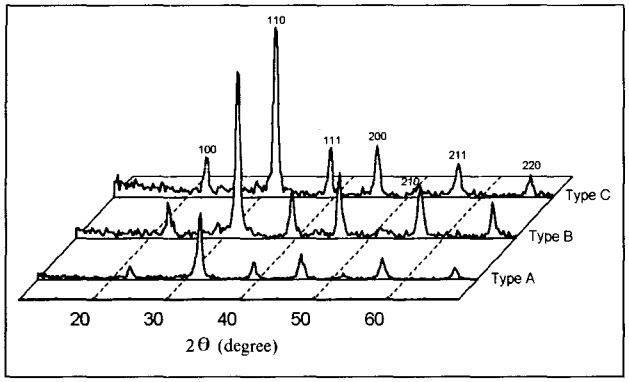

Fig. 3 X-ray diffraction patterns of (a) BST thin films A, (b) B and (c) C heat-treated at 750℃.

Surface conditions of the BST thin film C deposited on the Pt/Ta/SiO_2/Si substrates were observed by using the optical microscope at the magnification of 400 and are shown in Fig. 4. The surface micrograph of the film on Pt/Ta/SiO_2/Si substrate shows a relatively clean surface condition without hillocks.

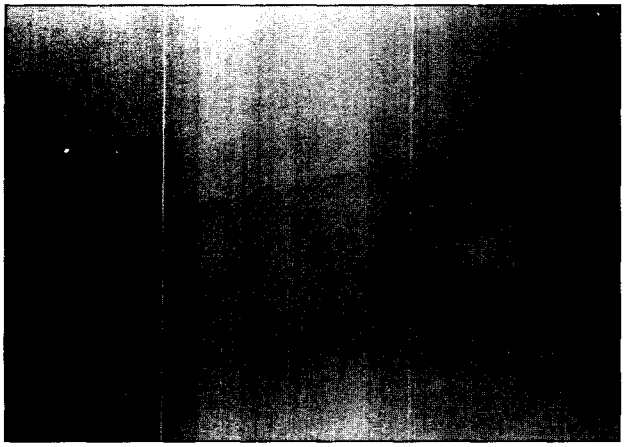

Fig. 4 Optical photographs of BST thin film C deposited on Pt/Ta/SiO_2/Si substrates.

Dielectric constant and loss tangent for each BST (70/30) thin film made from the solution B and the solution C are shown in TABLE II. Comparison between the properties of the film B and those of the film C shows that film C has the better dielectric properties than the film B. At the test frequency of 10kHz, dielectric constant and loss tangent of the film C are 339 and 0.052, respectively whereas those of the film B are 286 and 0.052, respectively.

TABLE II Dielectric Constant and Loss Tangents for the BST Thin Films (at 10kHz).

	Dielectric constant	Loss tangent
Type B	286	0.052
Type C	339	0.052

We measured the I-V characteristics of the films B and C. In the voltage range lower than 5V, the film B shows the smaller leakage current density than the film C, but it has the higher increasing rate. Hence the voltage range higher than 5V, the film B shows the larger leakage current density than the film C. The measured leakeage current density is summarized and exhibited in TABLE III. At the measurement voltage of 3V, the leakage current densities of the film B and of the film C are 7.2 and 13.3μA/cm^2, respectively.

TABLE III Leakage Current Density of the BST Thin Films (at 3V).

	Leakage Current Density (μA/cm^2)
Type B	7.2
Type C	13.3

IV. CONCLUSION

We have evaluated three different BST sol-gel solutions prepared by using different solvents with or without an additive. Barium-acetate, strontium-acetate and titanium isopropoxide used as the starting materials and acetic acid was used as the solvent of barium acetate and strontium acetate for all three solutions. For solution A, acetic acid was also used as the solvent of titanium isopropoxide and no additive was added. For solution B, 2-methoxyethanol was used as the solvent of titanium isopropoxide and no additive was added. Solution C was same as the solution B except having an additive of ethylene glycol. Solution A showed white precipitates after ageing of a couple of days and the film made from this solution showed severe cracks on the surface. Solution B and solution C showed the excellent stability and remained homogeneous even after a month of ageing. They were proved to produce excellent films without cracks. An interesting phenomenon was observed when fabricating the films on the substrate. BST films deposited on the Pt/Ta/SiO_2/Si substrate did not show the hillocks on the surface. Comparison between the dielectric properties of the film B and those of the film C shows that the film C has the better dielectric properties. This may be due to the beneficial effect of the ethylene glycol which makes the solution more stable by forming chelate derivatives. The BST(70/30) thin film made from solution C shows excellent dielectric properties. Its dielectric constant, loss tangent at 10kHz and leakage current density at 3V are 339, 0.052 and 13.3μA/cm^2, respectively.

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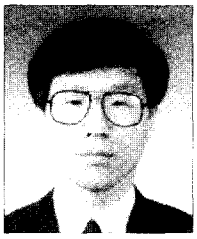

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