PREPARATION OF A NEW $SrBi_2Ta_2O_9$ (SBT) CHEMICAL SOLUTION USING CROWN ETHER AND ITS THIN FILM DEPOSITION

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ABSTRACT

A new chemical solution for the deposition of $SrBi_2Ta_2O_9$ (SBT) thin films using crown ether is proposed. Crown ether enhances the solubility of bismuth acetate in acetic acid, which makes a solvent solution possible. A metal acetate-based SBT precursor solution was prepared in acetic acid using 18-crown-6, strontium acetate, bismuth acetate and tantalum ethoxide. (115)-preferentially oriented ferroelectric SBT thin films were formed on $Pt/TiO_2/SiO_2/Si$ substrates by spin-coating with the new solution. After post-annealing at 800℃, a hysteresis loop obtained from a 2000Å thick SBT film with Pt electrodes showed a remanent polarization of ~3μC/cm^2 and a coercive voltage of ~50kV/cm. It was shown from SIMS depth profiles that excess bismuth atoms in the SBT thin film diffused towards the Pt electrodes during post-annealing.

INTRODUCTION

Ferroelectric thin films have been studied for possible applications in non-volatile memory devices, especially PZT (Lead zirconium titanate) has been used as a capacitor material in ferroelectric random access memory (FRAM) fabrication. PZT thin films have good material properties such as a high dielectric constant, large remanent polarization and low process temperature. However, severe polarization fatigue with metal contacts and retention problems remain as ongoing material issues for PZT thin films.[1] Recently, the bismuth layer-structured ferroelectric material $SrBi_2Ta_2O_9$ (SBT) has attracted attention as a prime candidate for replacing PZT in FRAM technology [2,3,4,5] owing to its excellent fatigue endurance and low coercive voltage. However, shortcomings of SBT thin films such as a relatively high formation temperature (~800℃), low remanent polarization (P_r), high porosity and surface roughness still exist. SBT thin films can be deposited by sputtering[6], Pulsed Laser Deposition (PLD)[4], MOCVD[7,8,9], and Chemical Solution Deposition (CSD).[10,11,12,13] Among them, CSD is the most reproducible and simplest process developed so far for obtaining high quality ferroelectric thin films.

The chemical solution for SBT thin film preparation generally consists of three metal precursors and solvents to dissolve the metal precursors in a solution. In the well-known

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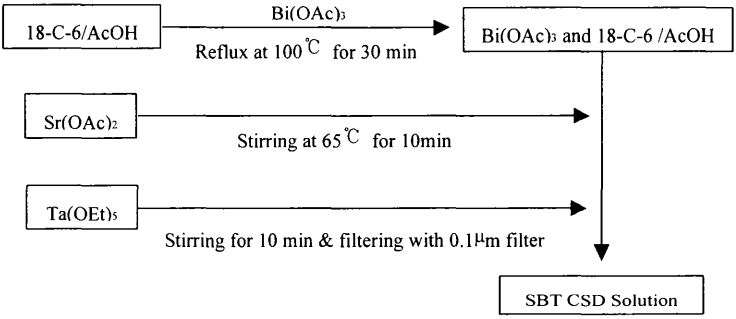


Fig. 1. Schematic diagram of preparing SBT precursor solution

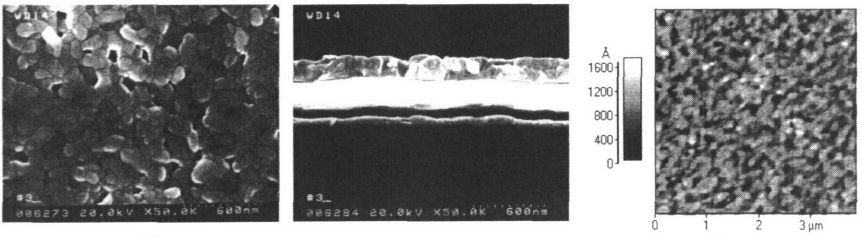
chemical solution preparation process for SBT films of Symetrix Corp., a metal 2-ethylhexanoate/xylene system was utilized with a composition of 20~30% excess bismuth precursor and 20~30% deficient strontium precursor solution. The films were annealed at high temperatures of ~ 800℃[12,13] and again post-annealed above 700℃ after top electrode deposition to get high quality ferroelectric properties. However, the films show high leakage current, rough surface morphology and a lot of pinholes on the surface. Several chemical routes for SBT thin films are also studied by Sharp[14], NEC[15], Mitsubish[16], Oki Electric Industry[17], Virginia Tech[7,9], Sandia National Labs[11] and so on. No single solution satisfying all requirements of SBT thin films for FRAM technology has yet been developed.

Boyle[11] and coworkers of Sandia National Labs utilized bismuth acetate [$Bi(OAc)_3$, Ac = $C(O)CH_3$], strontium acetate [$Sr(OAc)_2$] and tantalum ethoxide [$Ta(OEt)_5$, Et = CH_2CH_3] in a co-solvent of acetic acid and pyridine because of poor solubility of bismuth acetate in acetic acid. They mentioned $Bi(OAc)_3$ could not be solubilized by any combination of $Sr(OAc)_2$ or $Ta(OEt)_5$, heating or other solvents except pyridine.

In this study, we introduce a novel chemical solution based on acetate/alkoxide in acetic acid using crown ether and show the possibility of new solution route for obtaining high quality SBT thin films.

EXPERIMENT

The precursor solution used in this study for SBT thin film fabrication was prepared by the following procedures as shown in Fig. 1. 18-crown-6, $(CH_2CH_2O)_6$ (0.792g, 3.00mmol), was dissolved in acetic acid (5ml) and bismuth acetate, $Bi(OAc)_3$ (0.965g, 2.50mmol), was added into the same acetic acid solution. The solution was refluxed at 100℃ for 30 minutes with stirring. The bismuth acetate was then homogeneously dissolved in the18-crown-6/acetic acid solution. Strontium acetate, $Sr(OAc)_2$ (0.180g,



(a) (b) (c)

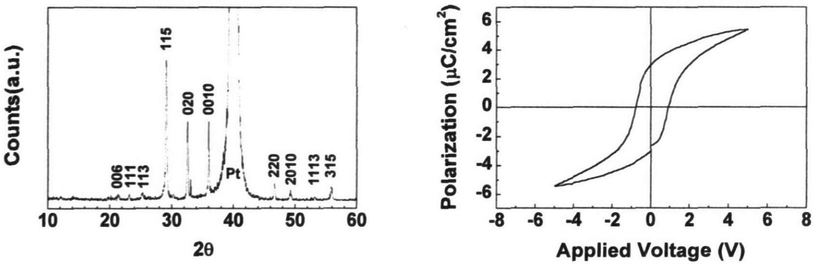
Fig. 2. Surface (a) and cross sectional (b) SEM of the baked and annealed SBT thin film; Surface AFM image of the same film (c).

0.88mmol), was added to the solution and stirred at 65℃ for 10 minutes. Tantalum ethoxide, $Ta(OEt)_5$ (0.774g, 1.91mmol), was subsequently added and stirred at room temperature for 10 minutes. All procedures were performed in air. Commercially available reagents below were used : 18-crown-6 (Aldrich, 99.5%), $Bi(OAc)_3$ (Strem Chemical, 99%), $Sr(OAc)_2$ (Strem Chemical, reagent grade), $Ta(OEt)_5$ (Strem Chemical, 99.99%), AcOH (Aldrich, glacial).

The substrates for spin-coating were prepared by the following procedures. TiO_2 films were sputtered onto thermally oxidized silicon wafers. Pt thin films were then deposited by DC magnetron sputtering and SBT thin films were deposited on Pt(1800Å)/TiO_2(300 Å)/SiO_2(2000Å)/Si substrates. The thickness of each layer was determined by cross sectional SEM. The precursor solution was injected on the substrates through 0.1μm filter and spin-coating was performed one time at 3500 rpm for 30 seconds in air. The spin-coated layer was baked on a hot plate at 300℃ for 5 minutes and then annealed at 800℃ for 30 minutes under a flowing atmosphere of oxygen (5 liters/minute). The thickness of the SBT thin film was 2000Å after annealing as shown in Fig. 2.

To estimate ferroelectric properties of the SBT thin films, capacitors were fabricated by depositing Pt top electrodes using a shadow mask. The thickness and area of the top electrodes were about 1000Å and 7.85×10^{-5} cm^2 (diameter : 100μm), respectively. After post-annealing at 800℃ for 15 minutes in oxygen atmosphere, the ferroelectric response of the film was measured with a RT66A ferroelectric tester (Radiant Technologies). The microstructure of the SBT thin film prepared from the new chemical solution was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), secondary ion mass spectroscopy (SIMS) and X-ray diffraction (XRD) technique.

This study was designed to investigate the possibility of a metal acetate/crown ether/acetic acid system as a precursor solution for SBT thin films, so the procedures and process conditions of solution preparation and capacitor fabrication were not optimized and followed general conditions of Boyle's methods.[11]



(a) (b)

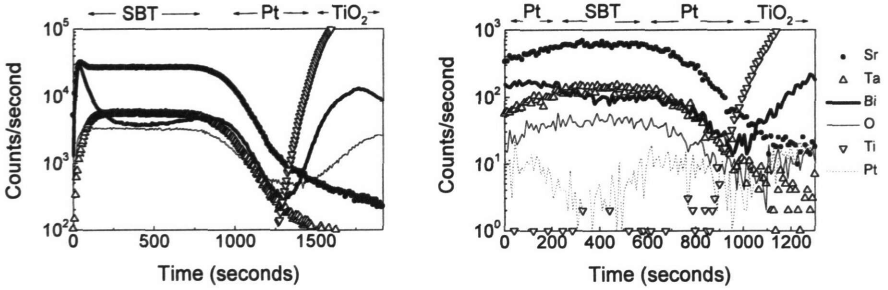
Fig. 3. XRD spectrum (a) and hysteresis loop (b) of the ferroelectric SBT thin films.

RESULTS AND DISCUSSION

Bismuth acetate has a polymeric crystal structure in the solid state.[18] This means that acetate ligands coordinated to the bismuth ion interact with adjacent bismuth ions, thus forming intermolecular bonds, which lead to polymeric structure and poor solubility in acetic acid or general organic solvents. However, in the new solution, crown ether is introduced to spatially surround the bismuth cation, therefore, it is expected that intermolecular interactions between bismuth ions and neighboring acetate ligands are blocked. This modification increases the solubility of bismuth acetate in organic solvents. 18-crown-6, one of the crown ethers, is a cyclic ether shaped like a crown of 2.6-3.2 Å diameter and has 6 oxygen atoms to donate electrons into the coordination sphere of metal ions. Therefore Bi^{3+} ions of ~1.92 Å diameter can effectively be surrounded by 18-crown-6 and blocked from intermolecular interactions.

In fact, bismuth acetate was reported to be sparingly soluble in general organic solvents except for amines[11] at room temperature but could be further dissolved in acetic acid by heating, although precipitating again at room temperature. However, in the SBT precursor solution modified by 18-crown-6, bismuth acetate remained homogeneously dissolved even at room temperature. Such an increase of solubility can be explained by the fact that 18-crown-6 acts as a Lewis base which can surround or isolate bismuth ions from neighboring acetate ligands.

The SBT thin film prepared from our new chemical solution showed grains of ~1000Å diameter and pinholes of 1000~1200Å depth. Average roughness measured by AFM was ~190Å as shown in Fig. 2(c). The morphology of the SBT thin film was similar to Symetrix's films rather than Sandia National Lab's. Since the solution was viscous and concentrated, when the film of ~2000 Å thickness was formed by one time spin-coating, the morphology of the film could be improved by optimizing the viscosity and the concentration of the solution as well as the thin film formation process.



(a) (b)

Fig. 4. SIMS depth profiles of SBT thin film ; (a) before post annealing (no top electrode), (b) after post annealing (Pt top electrode deposited).

Generally, it is well known that SBT thin films have a Bi-deficient pyrochlore phase due to the evaporation of bismuth from the films during the annealing process. Therefore, the composition of metal precursors in the solution was designed to prevent the formation of a bismuth-deficient pyrochlore phase in the SBT thin film. Sufficient bismuth acetate was induced to be ~ 40 % excess (Sr : Bi : Ta = 1 : 2.8 : 2.2). The XRD spectrum in Fig. 3(a) shows that the SBT thin film has perovskite structure of (115)-preferred orientation which contributes to its ferroelectricity. Pyrochlore phase is hardly visualized in the XRD spectrum.

As shown in the SIMS depth profile of Fig. 4(a), before post-annealing, a lot of bismuth atoms that diffused towards the surface or bottom electrode were detected in the surface region and TiO_2 layer, respectively. Therefore, it is thought that the surface region of the SBT film is bismuth-rich and may not be completely the ferroelectric phase before post-annealing. On the other hand, as can be seen from Fig. 4(b), after Pt top electrode deposition and post-annealing at 800℃ for 15 minutes, excess bismuth atoms in the interfacial regions of the Pt/SBT/Pt structure diffused towards the Pt electrodes. As a result, the ferroelectric perovskite structure of the SBT film was uniformly accomplished and the hysteresis loop of the Pt/SBT/Pt capacitor was obtained as shown in Fig. 3(b). The ferroelectric properties were measured to be ~3μC/cm^2 of remanent polarization and ~50kV/cm of coercive voltage. The loop was saturated at ~5V.

CONCLUSIONS

A new chemical solution for ferroelectric SBT thin films was prepared from metal acetate and ethoxide in only acetic acid by using crown ether to increase the solubility of bismuth acetate. (115)-preferentially oriented ferroelectric SBT thin films were formed on Pt/TiO_2/SiO_2/Si substrates with the new solution. After the deposition of the Pt top electrode and post-annealing, the ferroelectric properties of the Pt/SBT/Pt capacitors were measured to be: remanent polarization (P_r) ~3μC/cm^2 and coercive voltage (V_c) ~50kV/cm. It was shown from SIMS depth profiles that excess bismuth atoms in the SBT thin film diffused towards the Pt electrodes during post-annealing. Although the concentration and composition of the solution and the process conditions of the thermal treatment need to be optimized to improve the film properties, It is proved that the application of crown ether is a promising route to improve the solubility of insoluble metal precursors.

REFERENCES

1. T. Mihara, H. Watanabe and C.A. Paz de Araujo, *Jpn. J. Appl. Phys.* **33**, 5281 (1994).
2. H.N. Al-Shareef, D. Dimos, T.J. Boyle, W.L. Warren, and B.A. Tuttle, *Appl. Phys. Lett.* **68**, 690 (1996).
3. K. Amanuma, T. Hase and Y. Miyasaka, *Appl. Phys. Lett.* **66**, 221 (1995).
4. R. Dat, J.K. Lee, O. Auciello and A.I. Kingon, *Appl. Phys. Lett.* **67**, 572 (1995).
5. C. A-Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott and J.F. Scott, *Nature* **374**, 627 (1995).
6. J. Im, A.R. Krauss, A.M. Dhote, D.M. Gruen, O. Auciello, R. Ramesh, and R.P.H. Chang, *Appl. Phys. Lett.* **72**, 2529 (1998).
7. Y. Zhu, S.B. Desu, T. Li, S. Ramanathan and M. Nagata, *J. Mater. Res.* **12**, 783 (1997).
8. N.J. Seong, S.G. Yoon and S.S. Lee, *Appl. Phys. Lett.* **71**, 81 (1997).
9. T. Li, Y. Zhu, S.B. Desu, C.H. Peng and M. Nagata, *Appl. Phys. Lett.* **68**, 616 (1996).
10. P.C. Joshi, S.O. Ryu, X. Zhang and S.B. Desu, *Appl. Phys. Lett.* **70**. 1080 (1997).
11. T.J. Boyle, C.D. Buchheit, M.A. Rodriguez, H.N. Al-Shareef, B.A. Hernandez, B. Scott and J.W. Ziller, *J. Mater. Res.* **11**, 2274 (1996).
12. H. Watanabe, T. Mihara, H. Yoshimori and C.A. Paz de Araujo, *Jpn. J. Appl. Phys.* **34**, 5240 (1995).
13. T. Atsuki, N. Soyama, T. Yonezawa and K. Ogi, *Jpn. J. Appl. Phys.* **34**, 5096 (1995).
14. N. Ogata, M. Nagata, K. Ishihara, H. Urashima, A. Okutoh, S. Yamazaki, S. Mitarai and J. Kudo, *Jpn. J. Appl. Phys.*. **37**, 3481 (1998).
15. K. Amanuma, T. Hase and Y. Miyasaka, *Jpn. J. Appl. Phys.* **66**, 221 (1995).
16. T. Atsuki, N. Soyama, T. Yonezawa and K. Ogi, *Jpn. J. Appl. Phys.* **34**, 5096 (1995).
17. I, Koiwa, T. Kanehara, J. Mita, T. Iwabuchi, T. Osaka, S. Ono and M. Maeda, *Jpn. J. Appl. Phys.* **35**, 4946 (1996).
18. S.I. Troyanov and A.P. Pisarevsky, *Koord. Khim.* **17**, 909 (1991).