Transactions of the Materials Research Society of Japan 29[4] 1105-1108 (2004)

Synthesis of Perovskite Oxide Films for Memory Applications

T. Matsumoto, A. Niino, S. Baba[1], H. Saito[2], K. Numata[2] and S. Miyake
Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki 567-0047, Japan
Fax: 81-6-6879-8661, e-mail: matutake@jwri.osaka-u.ac.jp
[1]National Institute of Advanced Industrial Science and Technology (AIST), Japan
[2]Kanagawa High-Technology Foundation (KTF), Japan

Perovskite oxide films of $SrTiO_3$ (STO), $(Ba,Sr)TiO_3$ (BST) and $SrBi_2Ta_2O_9$ (SBT) were prepared on Si(100) and $Pt/Ti/SiO_2/Si$ substrates by mirror-confinement-type electron cyclotron resonance (MCECR) plasma sputtering with Ar or mixture of Ar and O_2. The obtained films were annealed by millimeter-wave and electric furnace. As-deposited STO films sputtered on $Pt/Ti/SiO_2/Si$ substrates in the mixed gas of Ar and O_2 were crystalline even though the substrates were kept at a low temperature below 450K during deposition. SBT films on $Pt/Ti/SiO_2/Si$ were also crystallized by electric furnace annealing at 873K, which is lower than typical temperatures for crystallization of the film prepared by chemical solution method. STO and BST films annealed by millimeter-wave were crystallized at lower temperatures than those by electric furnace. For crystallized STO films on Si, a diffraction peak derived from SiO_2 was not found in films annealed by millimeter-wave because of a low annealing temperature, while this peak was observed in those by electric furnace. Crystalline size of a BST film annealed at 773K by millimeter-wave was as large as that at 923K by electric furnace. The STO and BST films annealed by millimeter-wave exhibited quite high relative dielectric constant of 260 and 600, respectively.
Key words: mirror-confinement-type ECR plasma sputtering, millimeter-wave heating, perovskite, low temperature synthesis

1. INTRODUCTION

Perovskite oxide films, such as STO, BST, and SBT, have attracted much attention for their applications to next generation memories. STO and BST are candidate materials for G-bit DRAM (Dynamic Random Access Memory) while SBT is for FeRAM (Ferroelectric Random Access Memory). These films have been synthesized by magnetron sputtering [1, 2], MOCVD (Metal-organic Chemical vapor deposition) [3, 4], Pulsed laser deposition [5, 6], and CSD (Chemical Solution Deposition) [7, 8]. In order to achieve good electrical properties of the films, though, they must be crystalline and a heat treatment at a high temperature is necessary for their crystallization. CMOS (Complementary Metal Oxide Semiconductor transistor) and other structures are spoiled or even destroyed by the heat treatment and lowering this temperature is strongly desired.

Utilization of plasma is considered to be one of hopeful methods to solve the problem because ions and excited particles can be helpful in synthesizing films. MCECR plasma sputtering is a method to deposit films with the use of higher plasma density in a low pressure around 10^{-2} Pa than conventional magnetron plasma.

Millimeter-wave heating is reported to have a positive effect as a new material process. Ceramics were successfully sintered at lower temperatures than conventional electric furnace heating [9, 10]. These results mean that millimeter-wave heating has a potential to reduce the temperature for the improvement of the film characteristics.

In this study, we report STO, BST and SBT films prepared by these two promising methods: MCECE plasma sputtering and millimeter-wave heating.

2. EXPERIMENTAL

Figure 1 shows a schematic illustration of MCECR plasma sputtering apparatus [11]. It consists of a vacuum chamber, two electromagnetic coils, two cylindrical target holders, a microwave source, an RF power source, and a substrate holder. The coils form a mirror magnetic field. A cylindrical sputtering target was set on the right target holder as shown in the figure, and the three targets have compositions of $SrTiO_3$, $(Ba_{0.5},Sr_{0.5})TiO_3$, and $Sr_{1.0}Bi_{2.2}Ta_{2.0}O_{9+x}$. After evacuating the gas in the chamber below 1.3×10^{-4} Pa, Ar or Ar and O_2 gas

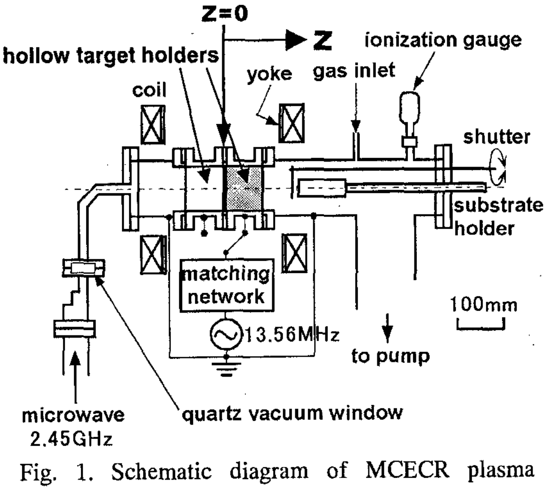

Fig. 1. Schematic diagram of MCECR plasma sputtering apparatus.

mixture was flowed into the chamber to a pressure of 2.7×10^{-2} Pa for STO and BST, and 6.7×10^{-2} Pa for SBT. The RF power of 100W was supplied to the target in order to sputter it, while the 2.45GHz microwave power of 200W was used for production of the plasma. For SBT, a cylindrical Ta target was also set on the left target holder, and DC bias of -80 to -100V was applied to it in order to increase a Ta content to the film composition. Films were deposited on Si(100) and Pt(200nm)/Ti(50nm)/SiO_2/Si substrates which were maintained at a floating potential without substrate heating. Thickness of the films was about 100-200nm. After the deposition of the films, they were annealed for 60min in ambient air for STO and BST, and in 0.1MPa O_2 atmosphere for SBT by 28GHz millimeter-wave and electric furnace heating.

Crystal structures were analyzed with an X-ray diffractometer (XRD). Film thickness was measured by mechanical stylus method. Electrical properties of the films were measured with a ferroelectric test system. For the measurement, Pt top electrodes 0.20-0.35mm in diameter were deposited on the films through a metal shadow mask by electron beam evaporation after the film annealing mentioned above. For SBT films, recovery annealing in O_2 by electric furnace was conducted after the Pt top electrode deposition.

3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of as-deposited STO films prepared on Pt/Ti/SiO_2/Si substrates at various sputtering gas ratios of Ar/O_2. The film prepared at Ar/O_2=100/0 is amorphous, whereas the other four films which were prepared with sputtering gas including oxygen were crystalline, and the STO peaks become sharper as the oxygen content of the sputtering gas increases. This indicates that oxygen plays an important role in crystallization of STO probably because oxygen deficiency inhibits the film from crystallizing. A similar XRD result was observed in BST film synthesis. We must note here that the STO films are crystalline in spite of the fact that the substrates were kept at a low temperature below 450K during the deposition and no heat treatment was conducted for the films after the deposition. We can conclude that MCECR plasma sputtering greatly reduces the process temperature for crystalline STO film synthesis. These films are expected to exhibit good properties because they were not treated with a high temperature process which causes films to deteriorate owing to atomic diffusion between STO and Pt layers.

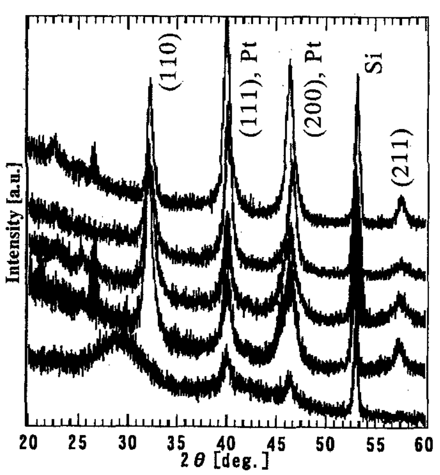

Fig. 2. XRD patterns of as-deposited STO films which were prepared on Pt/Ti/SiO_2/Si substrates at various sputtering gas ratios of Ar/O_2.

XRD patterns were measured for SBT films which were deposited on Pt/Ti/SiO_2/Si substrates under various sputtering conditions and annealed by electric furnace. It was found that all as-deposited films were amorphous, and required annealing temperature for turning the amorphous into the layered perovskite structure was in most cases 873K, which is lower than typical temperatures for crystallization of the film by chemical solution method which is widely employed for SBT film synthesis.

Figure 3 shows a change in XRD patterns of SBT films on Pt/Ti/SiO_2/Si substrates according to the sputtering gas ratio of Ar/O_2. They were prepared with a Ta target bias of –100V and annealed at 973K by

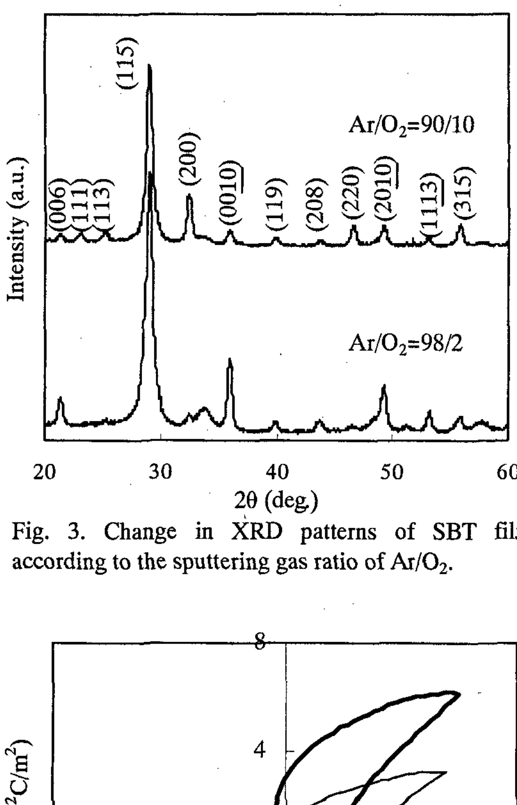

Fig. 3. Change in XRD patterns of SBT films according to the sputtering gas ratio of Ar/O_2.

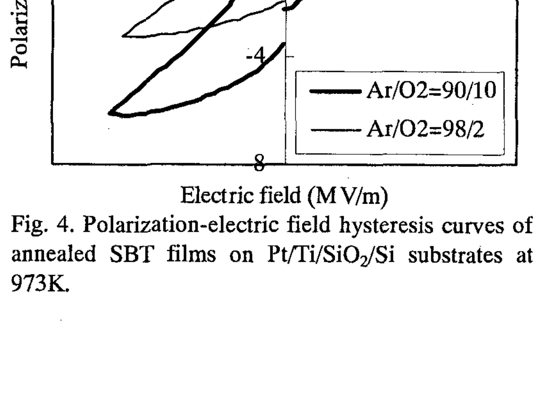

Fig. 4. Polarization-electric field hysteresis curves of annealed SBT films on Pt/Ti/SiO_2/Si substrates at 973K.

electric furnace. The peak intensity of (00<u>10</u>) is higher than that of (200) in the film prepared at Ar/O_2=98/2, while the two intensities are the opposite at Ar/O_2=90/10. SBT films with c-axis orientation were reported to exhibit no remnant polarization [12, 13], therefore the film prepared at Ar/O_2=90/10 is expected to have larger remnant polarization than that at Ar/O_2=98/2. MCECR plasma sputtering can control the orientation easily, while such control is difficult by chemical solution method.

Figure 4 shows polarization-electric filed hysteresis curves of SBT films prepared at Ar/O_2=98/2 and 90/10, and annealed at 973K by electric furnace. As expected from the film orientation shown in Fig. 3, the film prepared at Ar/O_2=90/10 have larger remnant polarization than that at Ar/O_2=98/2. Since Ar/O_2 ratio was reported to have almost no effect on a film composition [14], this difference in remnant polarization is due to the orientation difference. A well-saturated hysteresis curve was obtained in the film at Ar/O_2=90/10.

We investigated effects of millimeter-wave annealing on those perovskite films. Figure 5 shows XRD patterns of STO films which were prepared on Si(100) substrates at a sputtering gas ratio of Ar/O_2= 100/0 and annealed by millimeter-wave and electric furnace at various temperatures. The as-deposited films are amorphous. It is found that STO films annealed by millimeter-wave are crystallized at 623K, whereas those by electric furnace are crystallized at 673K. In addition to this reduction in crystallization temperature, the broad peak ranging from 2θ=40 to 45 degree in the films annealed by electric furnace is not seen in that by millimeter-wave. Since the same broad peak was observed in a Si substrate annealed at 923K by millimeter-wave, the peak is considered to come from SiO_2 which was formed on a surface of the substrate by oxidation. It is concluded that millimeter-wave annealing is effective for an STO crystallization temperature reduction which leads to suppression of oxygen diffusion from STO to Si.

A similar phenomenon was observed in BST film annealing. Figure 6 shows XRD patterns of BST films which were deposited on $Pt/Ti/SiO_2/Si$ substrates at a sputtering gas ratio of Ar/O_2=70/30 and annealed by millimeter-wave and electric furnace at various temperatures. It is found that BST films are crystallized at temperatures more than 723K by millimeter-wave annealing, while the film annealed at 773K by electric furnace is not crystallized sufficiently. Note that the broad peak seen in Fig. 5 does not appear because of deposition on $Pt/Ti/SiO_2/Si$ substrates. Crystalline size was measured from full-width at half-maximum (FWHM) of the BST(110) peak, and the size for a film annealed at 773K by millimeter-wave was found to be as large as that at 923K by electric furnace.

Relative dielectric constant of STO and BST films were measured. An as-deposited STO film prepared on a $Pt/Ti/SiO_2/Si$ substrate at Ar/O_2=50/50 exhibited a value of about 70, while a film annealed at 623K by millimeter-wave showed 260, which is very close to the value for STO bulk. An as-deposited BST film prepared on a $Pt/Ti/SiO_2/Si$ substrate at Ar/O_2=50/50 showed a value of about 50. The reason of this small value is that the film is amorphous as shown in Fig. 6. On the other hand, a film annealed at 873K by millimeter-wave showed a relatively high value of about 600. Millimeter-wave annealing is effective for improvement of film properties as well as lowering the crystallization temperature.

4. CONCLUSION

STO, BST and SBT films were prepared on Si(100) and $Pt/Ti/SiO_2/Si$ substrates by MCECR plasma sputtering, and annealed by millimeter-wave and electric furnace. As-deposited STO films sputtered on $Pt/Ti/SiO_2/Si$ substrates by mixed gas of Ar and O_2 were crystalline even though the substrates were kept at a low temperature below 450K during the deposition. SBT films on $Pt/Ti/SiO_2/Si$ were also crystallized by electric furnace annealing at 873K, which is lower than typical temperatures for crystallization of the film prepared by chemical solution method. STO and BST films annealed by millimeter-wave were crystallized at lower

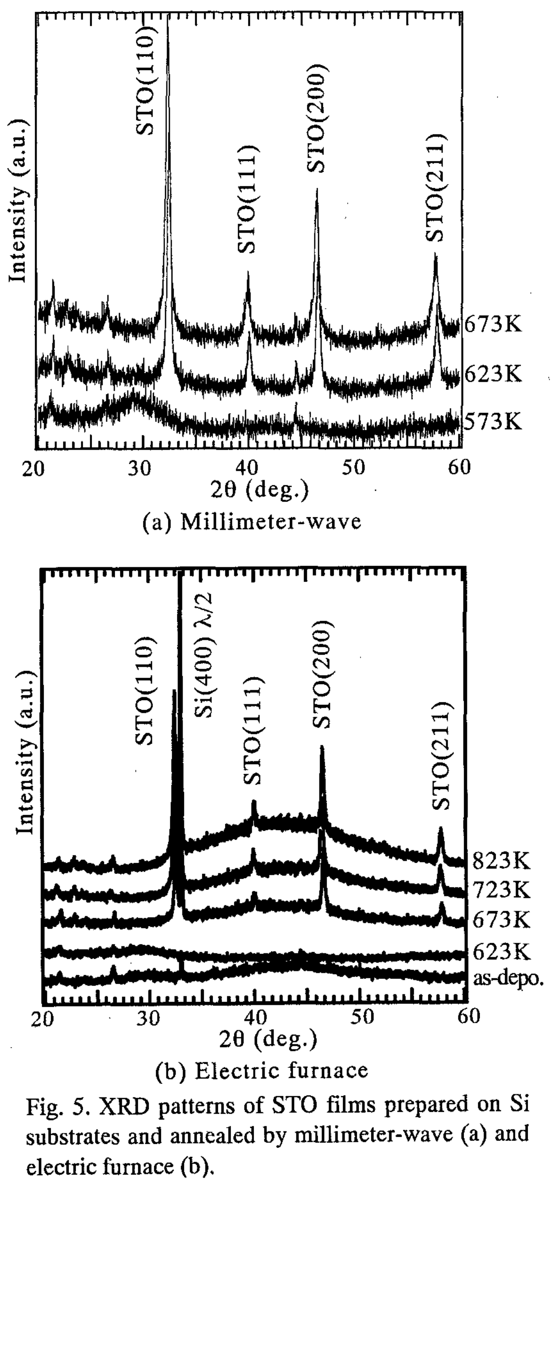

Fig. 5. XRD patterns of STO films prepared on Si substrates and annealed by millimeter-wave (a) and electric furnace (b).

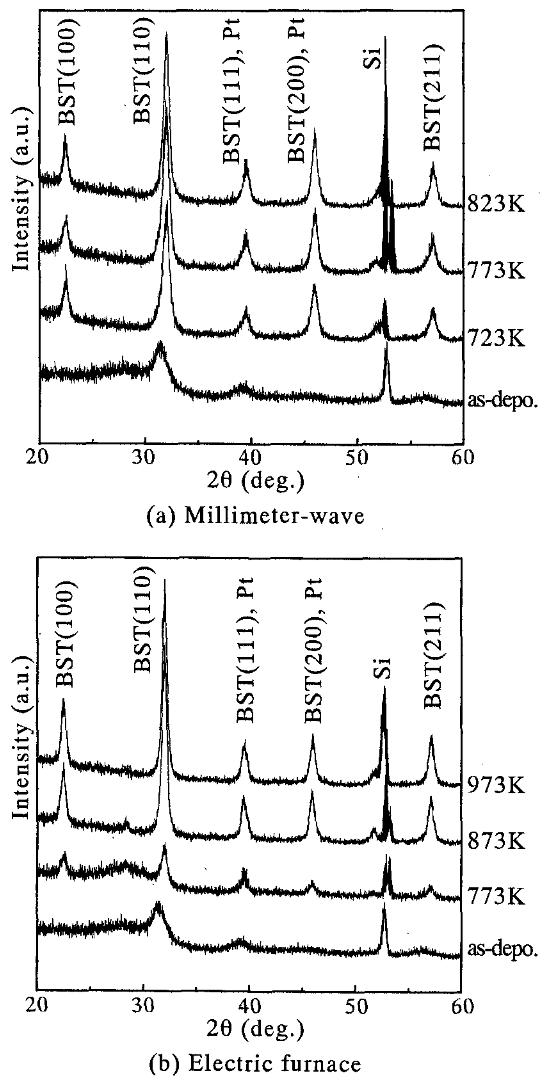

Fig. 6. XRD patterns of BST films prepared on Pt/Ti/SiO_2/Si substrates and annealed by millimeter-wave (a) and electric furnace (b).

temperatures than those by electric furnace. Crystalline size of a BST film annealed at 773K by millimeter-wave was as large as that at 923K by electric furnace. The STO and BST films exhibited quite high relative dielectric constant of 260 and 600, respectively.

REFFERENCES

[1] Z. Wang, U. Helmersson, L. D. Madse, I. P. Ivanov, P. Münger, S. Rudner, B. Hjörvarsson and J.-E. Sundgren, J. Vac. Sci. Technol., A17, 564-70 (1999).

[2] M. Matsuoka, K. Hoshino and K. Ono, *J. Appl. Phys.*, **76**, 1768-75 (1994).

[3] T. Kawahara, M. Yamamuka, T. Makita, J. Naka, A. Yuuki, N. Mikami and K. Ono, *Jpn. J. Appl. Phys.*, **5129-34** (1994).

[4] M. Mitsuya, N. Nukaga, T. Watanabe, H. Funakubo and K. Saito, Jpn. J. Appl. Phys., 40, L758-60 (2001).

[5] S. Saha and S. B. Krupanidhi, Mater. Sci. Eng. B57, 135-46 (1999).

[6] M. Noda, Y. Adachi, H. Sugiyama, T. Nakaiso and M. Okuyama, Appl. Phys., A71, 113-16 (2000).

[7] F. M. Pontes, E. J. H. Lee, E. R. Leite and E. Longo, *J. Mater. Sci.*, **35**, 4783-87 (2000).

[8] M. L. Calzada, A. González, R. Jiménez, C. Alemany and J. Mendiola, *J. Eur. Ceram. Soc.*, **21**, 1517-20 (2001).

[9] Z. Xie, J. Yang and Y. Huang, *Mater. Lett.*, **37**, 215-20 (1998).

[10] M. A. Janney and H. D. Kimrey, *Mat. Res. Soc. Symp. Proc.*, **189**, 215-27, 1991.

[11] S. Baba and S. Miyake, *Jpn. J. Appl. Phys.*, **39**, 4945-51 (2000).

[12] H. Funakubo, K. Ishikawa, T. Watanabe, M. Mitsuya and N. Nukaga, *Adv. Mater. Opt. Electron.*, **10**, 193-200 (2000).

[13] N. Fujimura, D. T. Thomas S. K. Streiffer and A. I. Kingon, *Jpn. J. Appl. Phys.*, **37**, 5185-88 (1998).

[14] M. S. Tsai, T. Y. Tseng, *Thin Solid Films*, **372**, 190-99 (2000).

(Received October 11, 2003; Accepted March 10, 2004)