Thin Solid Films 398–399 (2001) 652–656
www.elsevier.com/locate/tsf

Etch characteristics of $SrBi_2Ta_2O_9$ (SBT) thin films using magnetized inductively coupled plasmas

Young-Joon Lee[a,*], Chang-Hyun Jeong[a], Jeong-Woon Bae[a], In-Kyu You[b], Jong-Wan Park[c], Geun-Young Yeom[a]

[a]Department of Materials Engineering, Sungkyunkwan University, Jangan-Gu, Chunchun-Dong 300, Suwon, Kyunggi-do 440746, South Korea
[b]Micro-Electronics Technology Laboratory, ETRI, Yusong-Gu, Kajong-Dong 161, Daejon, South Korea
[c]Department of Metallurgical Engineering, Hanyang University, Seongdong-Gu, Haengdang-Dong 17, Seoul, South Korea

Abstract

In this study, $SrBi_2Ta_2O_9$ (SBT) thin films were etched using a magnetized inductively coupled plasma (MICP) and their etch characteristics were investigated as a function of Cl_2/Ar gas mixing ratio, inductive power and bias voltage. The SBT etch rate appeared to show the highest value when Cl_2 concentration in the Cl_2/Ar mixture was 30%, even though the SBT etch rate remained nearly constant when the Cl_2 concentration in the mixture was higher than 10%. SBT etch rates were also strongly influenced by both inductive power and bias voltage. This result implies that the etching of SBT is dependent upon both ion bombardment and chemical reaction. An etch rate of 150 nm/min could be obtained using 30% Cl_2/70% Ar, 6.7 Pa of operation pressure, 600 W of inductive power, and −300 V of bias voltage. The etch selectivity of SBT over Pt, and photoresist were less than 0.5 and 1.0∼1.2, respectively, when the Cl_2 was more than 10% in Cl_2/Ar mixtures. An SBT (200 nm)/Pt (100 nm)/Ti (100 nm) heterostructure was etched using the MICP with 30% Cl_2/70% Ar mixture, which resulted in an anisotropic etch profile without the formation of sidewall residue.

Keywords: Thin films; Etch rate; Magnetized inductively coupled plasma

1. Introduction

Since ferroelectric materials normally have extremely large dielectric constants, their use as non-switching capacitors in dynamic random access memories (DRAMs) is rapidly evolving [1–3]. Recent work emphasized the research on SBT-based [4–7] and PZT-based [7–9] ferroelectric random access memories (FeRAMs) and barium strontium titanate-based (BST) capacitor DRAMs. Strontium bismuth tantalate-based (SBT) memories provide a major advantage of yielding capacitors with suitable properties including negligible fatigue and imprint for FeRAMs. In the fabrication of non-volatile memory devices, dry etching of the ferroelectric thin films is an important issue for the pattern transfer. SBT is more difficult to etch even though it has many advantages for the next generation of FeRAMs. It has been reported that the plasma-etch rate of SBT is approximately 70% of that of a comparable PZT layer. Desu and Pan [10] reported the etching characteristics of SBT and $SrBi_2Ta_xNb_{2-x}O_9$ films using SF_6 and $CHClFCF_3$ in a conventional reactive ion etching (RIE) system and obtained etch rates of <20 nm/min. Lee et al. [11] investigated the etching behavior and damage recovery of SBT films in a magnetron-enhanced RIE system using $Ar/CF_4/O_2/Cl_2$ plasmas. They also reported relatively slow etch rates (<28 nm/min) at 65°C.

Post etch residue in addition to low etch rates is also an important factor affecting ferroelectric pattern transfer. Redeposition of the etched material on the sidewall of the etched films has been observed when fluorine-based gases [12] or chlorine-based gases [13] were used to etch ferroelectric/Pt-layered heterostructures. These

* Corresponding author. Tel.: +82-331-2907418; fax: +82-331-2907410.
E-mail address: leeyj@nature.skku.ac.kr (Y.-J. Lee).

0040-6090/01/$ - see front matter
PII: S0040-6090(01)01371-2

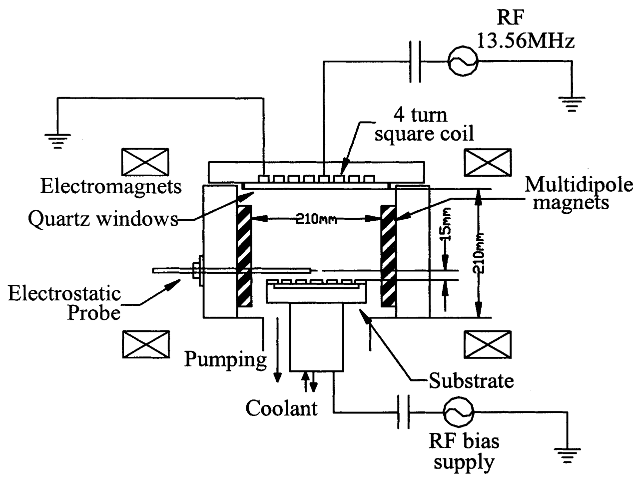

Fig. 1. Schematic view of the MICP etcher with Helmholtz type electromagnets and multidipole permanent magnets used in this experiment.

redeposited materials are not easily removed by post wet cleaning. However, with optimized chlorine-based gas combinations and a high-density plasma tool, it is possible to obtain residue-free etched surfaces in addition to high SBT etch rates.

Therefore, in this study, SBT etch rates and the selectivities over both the mask material (photoresist) and the electrode material (Pt) were studied as a function of Cl_2/Ar gas mixing ratio, inductive power and bias voltage using a MICP source which shows higher dissociation and ionization rates compared to a conventional inductively coupled plasma (ICP) source.

2. Experimental

A schematic view of the apparatus used in this study is shown in Fig. 1. A square array of magnet housing made of anodized aluminum was installed inside the chamber to hold permanent magnets having 3000 G on the magnet surface. The magnets were arranged in the housings to form a magnetic cusp. Fourteen pairs of equally spaced permanent magnets were inserted in the anodized aluminum housings. Square (500×500 mm) shaped helmholtz type axial electromagnets were also installed outside the chamber to supply 20 G of uniform external magnetic field inside the chamber. The ICP coil was made of an Au-coated 4-turn square coil of copper. Radio frequency power (13.56 MHz, 0–1200 W) was applied to generate inductively coupled plasmas, while different 13.56 MHz rf power was applied to the water heated (70°C) substrate to induce bias voltages to the wafer. A 24-mm-thick quartz plate was used to separate the square coil from the plasma region. More details of the system and its characteristics can be found elsewhere [14].

The SBT thin films used in this study were prepared by metal organic deposition (MOD) using a spin coating method. SBT films were coated on Pt (100 nm)/Ti (100 nm)/Si substrates and prebaked on a hot plate at 400°C for 10 min. Pre-baked films were annealed at 800°C for 30 min under oxygen atmosphere for crystallization. Details of the procedure can be found elsewhere [11]. Changes in film thickness were measured by stylus profilometry after the removal of the patterned photoresist. Etch profile was observed by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 2 shows the etch rate of SBT thin film and its etch selectivities over Pt and photoresist as a function of Cl_2/Ar when total flow rate was maintained at 30 sccm. Other process conditions such as inductive power to the source, bias voltage and total pressure, and substrate temperature were also maintained at 600 W, −150 V, 6.7 Pa, and 70°C, respectively. As shown in the figure, the etch rate of SBT increased rapidly with the increase of Cl_2 concentration in the Cl_2/Ar mixture. However, the etch rates remained practically constant when Cl_2 concentration in the mixture was higher than 10%, even though the highest etch of SBT appears to be obtained when 30% of Cl_2 was reached in the Cl_2/Ar mixture. The etch rate was approximately 86 nm/min and it was two times higher than that by pure Ar. This result implies that SBT is etched not only by ion bombardment but also by chemical reaction. $BiCl_3$ (b.p.: 441°C), $SrCl_2$ (b.p.: 1250°C) and $TaCl_5$ (b.p.: 233°C) are expected to form as etch products during the SBT

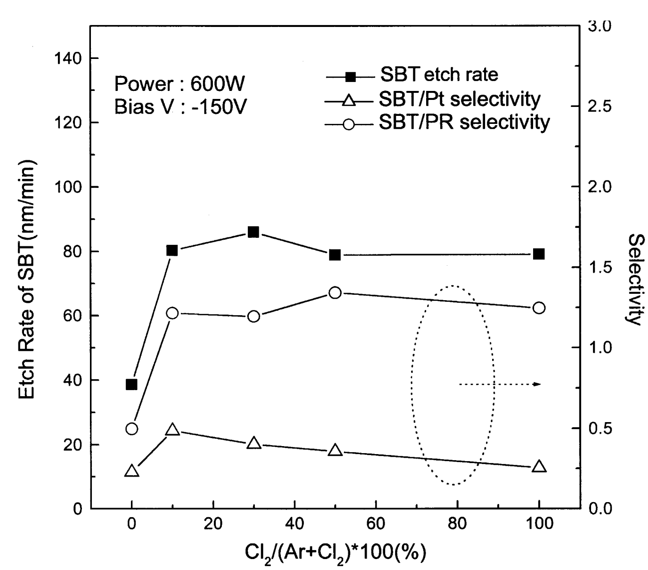

Fig. 2. SBT etch rate and its selectivities over Pt and photoresist as a function of Cl_2/Ar gas ratio in MICP. Process condition: 600 W of induction power; −150 V of bias voltage; and 6.7 Pa (30 sccm) of operation pressure.

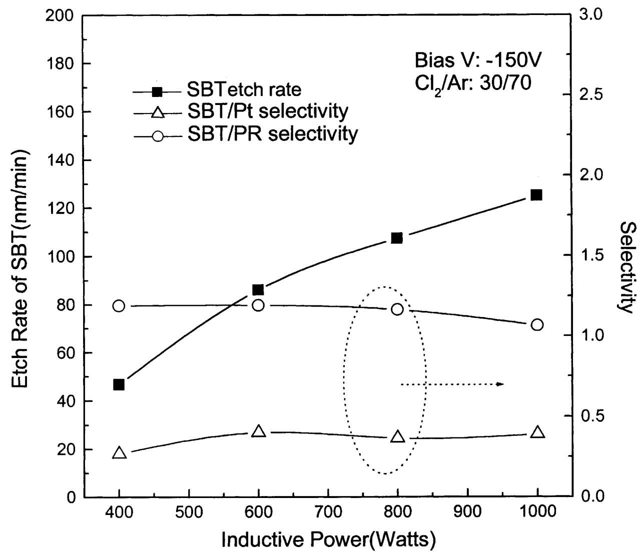

Fig. 3. The effects of MICP inductive power on the SBT etch rate and selectivities over Pt and photoresist. Process condition: 30% Cl_2/70% Ar; −150 V of bias voltage; and 6.7 Pa (30 sccm) of operation pressure.

etching with chlorine-based plasma chemistries. But, due to the low volatility of these chlorine compounds, the physical ion bombardment effect to enhance the ion assisted etch product desorption mechanism is indispensably required. Moreover, previous results of optical emission spectroscopy showed that the numbers of Cl_2^+ ions detected for MICP were approximately 2.5 times higher than those for conventional ICP at the same process conditions [15]. The increased Cl_2^+ ions in the plasma will increase the chemical and/or physical sputtering effect and the chemical reactivity during the SBT etching. The etch selectivity of SBT over photoresist increased from 0.5 to 1.2 when more than 10% of Cl_2 was mixed in Cl_2/Ar possibly due to the enhanced SBT etching by the formation of those high vapor pressure byproducts. The etch selectivity of SBT over Pt was generally lower than 0.5 possibly due to the similar enhanced etch mechanism of Pt in Cl_2/Ar by the formation of $PtCl_x$.

Fig. 3 shows the effect of inductive power on the etch rate of SBT and its etch selectivities over Pt and photoresist. 30% Cl_2/70% Ar gas combination was used in the experiment and other conditions were the same as those shown in Fig. 2. As shown in the figure, the increase of inductive power from 400 to 1000 W increased the SBT etch rate almost linearly from approximately 47 to 125 nm/min without saturation. The increase of SBT etch rate with the increase of inductive power appears to be from the increase of reactive chlorine radicals and ion density with the increase of inductive power, as investigated by a previous study for pure Cl_2 [14]. The etch rates of Pt and photoresist also increased linearly with the increase of inductive power due to the increase of reactive radicals and ion density. The highest etch rate of Pt at 1000 W of inductive power was 117 nm/min. Therefore, as shown in the figure, the etch selectivities of SBT over Pt and photoresist remained similar regardless of inductive power as 0.3–0.4 and 1.1–1.2, respectively. The highest SBT etch rates obtained in this experiment appear to be higher than those obtained by other researchers. In fact, the inductive coupled plasma source used in this experiment is a magnetized inductively coupled plasma source where axial Helmholtz type electromagnet is installed around the chamber and magnetic bucket type permanent magnets are installed inside chamber wall to enhance the etch rate and etch uniformity. Previous experiments [15,16] showed that the degree of ionization and dissociation was increased by increasing power transfer efficiency and by decreasing the loss of ions to the chamber wall when this type of magnet combination was used.

Fig. 4 shows the effect of dc-bias voltage on the etch rate of SBT and its etch selectivities over Pt and photoresist. The dc-bias voltage was varied from −100 to −300 V while keeping Cl_2/Ar gas mixture, inductive power, operational pressure and substrate temperature as 30% Cl_2/70% Ar, 600 W, 6.7 Pa, and 70°C, respectively. The increase of bias voltage from −100 to −300 V also linearly increased the SBT etch rate from 47 to 150 nm/min as shown in the figure. The increase of dc-bias appears to be more effective in increasing SBT etch rate than that by increasing inductive power, therefore, ion bombardment which enhances the removal of the byproducts formed on the surface in addition to physical

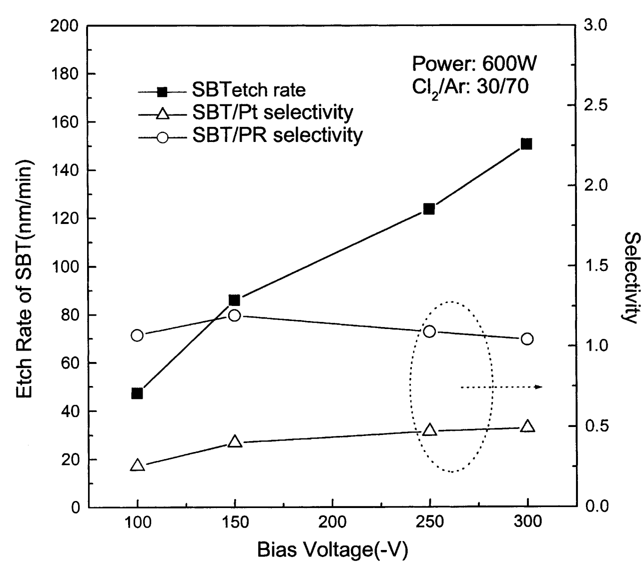

Fig. 4. The effects of dc-bias voltage on the SBT etch rate and its selectivities over Pt and photoresist. Process condition: 30% Cl_2/70% Ar; 600 W of inductive power; and 6.7 Pa (30 sccm) of operation pressure.

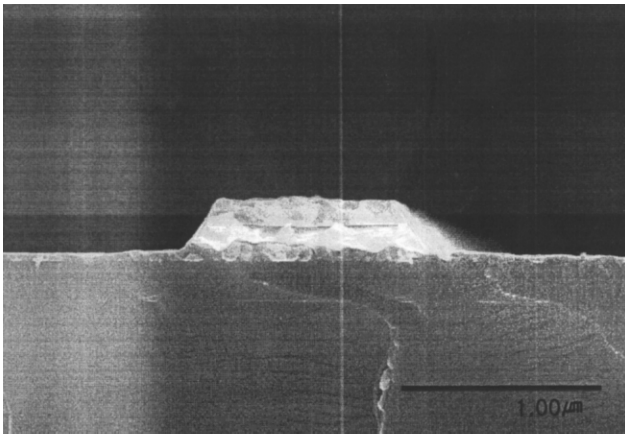

Fig. 5. Typical etch profile SBT/Pt/Ti film in the 30% Cl_2/70% Ar gas mixture. Process condition: 600 W of induction power; −150 V of bias voltage; and 6.7 Pa (30 sccm) of operation pressure.

sputtering appears to be one of the most important factors in the SBT etching. The etch selectivity of SBT over photoresist remained similar near 1.0, however, the etch selectivity of SBT over Pt appears to increase slightly with the increase of dc-bias voltage suggesting lower sensitivity of Pt etching on the ion bombardment. However, the etch selectivity also remained less than 0.5.

In the application of SBT, Pt is generally used as the electrode for SBT and Ti is used as the glue layer to the substrate, therefore, the multi-layer composed of SBT/Pt/Ti needs to be etched. To simplify the etching of the multi-layer, the SBT/Pt/Ti layer may need to be etched by one-step etching using one recipe without sacrificing the etch mask selectivity. However, due to the low SBT etch rate and low etch selectivity over photoresist, the previous research investigated using conventional low density reactive ion etching methods had to use a double metal mask such as Ti/Cr double layer. Also, even with high-density plasmas, sidewall residue was reported when fluorine-base or inadequate chlorine-base gas mixtures were used [17]. This sidewall residue remains as a fence after the removal of the photoresist and is difficult to remove even with post wet cleaning. Fig. 5 shows the etch profile of SBT (200 nm)/Pt (100 nm)/Ti (100 nm) deposited on the oxidized silicon wafer. 1.2-μm thick photoresist was used as the etch mask. Process condition was 30% Cl_2/70% Ar of gas mixture, 600 W of inductive power, −150 V of bias voltage, 6.7 Pa of operational pressure, and 70°C of substrate temperature. As shown in the figure, an SBT/Pt/Ti etch profile with reasonable anisotropy and with no sidewall residue could be obtained using a typical 1.2-μm photoresist when the magnetized inductively coupled plasma source and an optimized gas mixture were used.

4. Conclusions

In this study, the effects of process conditions such as Cl_2/Ar gas mixture, inductive power and bias voltage on the SBT etch rate and its selectivities over Pt and photoresist were investigated using a magnetized inductively coupled plasma source. Due to the relatively low vapor pressures of byproducts formed during the etching by Cl_2/Ar, ion bombardment in addition to chemical reaction was required to obtain high SBT etch rates. In this experiment, Cl_2 concentration of more than 10% in the Cl_2/Ar mixture enhanced SBT etch rates, and it appears to be from the formation of chlorides of Sr, Bi and Ta in SBT and the removal of those byproducts by physical sputtering. SBT etch rate increased linearly with the increase of inductive power and bias voltage, however, the increase of SBT etch rate was more sensitive to bias voltage. The etch selectivity of SBT over Pt was generally lower than 0.5 and that over photoresist was in the range from 1.0 to 1.2 when Cl_2 was mixed more than 10% in Cl_2/Ar. The highest SBT etch rate obtained in this experiment was 150 nm/min. When photoresist patterned SBT/Pt/Ti multi-layer was etched with 30% Cl_2/70% Ar, a reasonably anisotropic etch profile with no sidewall reside could be obtained.

Acknowledgements

This work was partially supported by the National Research Laboratory program (NRL) in Korea.

References

[1] R. Moazzami, C. Hu, W.H. Shepherd, IEEE Trans. Electron. Dev. 39 (1992) 2044.
[2] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Nature (Lond.) 401 (1999) 682.
[3] J.S. Lee, H.J. Kwon, Y.W. Jeong, H.H. Kim, S.J. Hyun, T.W. Noh, Appl. Phys. Lett. 74 (1999) 2690.
[4] O. Auciello et al., Phys. Today July (1998) 22.
[5] Y. Shimada, K. Arita, Y. Kato, K. Uchiyama, V. Joshi, M. Lim, Integrated Feroelectrics 34 (2001) 27.
[6] S.H. Kim, D.J. Kim, J. Im, S.K. Streiffer, O. Auciello, J.-P. Maria, A.I. Kingon, Integrated Feroelectrics 26 (1999) 253.
[7] O. Auciello, C.M. Foster, R. Ramesh, Annu. Rev. Mater. Sci. 28 (1998) 501.
[8] T. Davenport, S. Mitra, Integrated Feroelectrics 31 (2000) 213.
[9] G.R. Fox, S. Sun, T. Takamatsu, Integr. Feroelec. 31 (2000) 47.
[10] S.B. Desu, W. Pan, Appl. Phys. Lett. 68 (1996) 566.
[11] W.J. Lee, C.H. Shin, C.R. Cho, J.S. Lyu, B.W. Kim, B.G. Yu, K.I. Cho, Jpn. J. Appl. Phys. 38 (1999) 2039.
[12] J.J. van Glabbeek, G.A.C.M. Spierings, M.J.E. Ulenaers, G.J.M. Dormans, P.K. Larraon, Mater. Res. Soc. Symp. Proc. 310 (1993) 127.

[13] T. Shibano, T. Oomori, J. Vac. Sci. Technol. B 15 (1997) 1747.
[14] S.W. Hwang, Y.J. Lee, H.R. Han, J.B. Yoo, G.Y. Yeom, J. Vac. Sci. Technol. A 17 (1999) 1211.
[15] Y.J. Lee, H.R. Han, J. Lee, G.Y. Yeom, Surf. Coat. Technol. 131 (2000) 257.
[16] Y.J. Lee, H.R. Han, G.Y. Yeom, Surf. Coat. Technol. 133–134 (2000) 612.
[17] J.W. Seo, D.H. Lee, W.J. Lee, B.G. Yu, K.H. Kwon, G.Y. Yeom, E.G. Chang, C.I. Kim, J. Vac. Sci. Technol. A 18 (4) (2000) 1354.