2003년도 대한전기학회 전기물성·응용부문회 추계학술대회 논문집 (2003.10.31)

$BCl_3/Cl_2/Ar$ 플라즈마를 이용한 BST 박막의 식각 특성

김관하, 김동표, 김창일[*1], 이철인[2], 김태형[3]
중앙대학교 전자전기공학부[*1], 안산공과대학 전기과[2], 여주대학 전기시스템디자인과[3]

Etching characteristics of BST thin films using $BCl_3/Cl_2/Ar$ plasma

Gwan-Ha Kim, Dong-Pyo Kim, Chang-Il Kim[*1], Chul-In Lee[2], Tae-Hyung Kim[3]
School of Electrical and Electronics Engineering[*1], Dept. of Electrical Engineering[2], Dept. of Electric System Design[3]

Abstract - BST thin films were etched with inductively coupled plasmas. A chemically assisted physical etch of BST was experimentally confirmed by ICP under various gas mixtures. After a 20 % addition of BCl_3 to the Cl_2/Ar mixture, resulting in an increased the chemical effect. As a increases of RF power, substrate power, and substrate temperature, and decrease of working pressure, the ion energy flux and chlorine atoms density increased. The maximum etch rate of the BST thin films was 90.1 nm/min at the RF power, substrate power, working pressure, and substrate temperature were 700 W, 300 W, 1.6 Pa, and 20 ℃, respectively. It was proposed that sputter etching is dominant etching mechanism while the contribution of chemical reaction is relatively low due to low volatility of etching product.

1. INTRODUCTION

With the increasing density of memory devices, ferroelectric thin films that possess a high permittivity are of great interest for high-k dynamic random access memories (DRAMs). For DRAM application, the ferroelectric materials such as $Pb(Zr,Ti)O_3$ (PZT), $(Ba,Sr)TiO_3$ (BST), $SrBi_2Ta_2O_9$(SBT) appear to be the leading candidates among all other materials for the dielectric layer entering the capacitors. Among the various dielectric films, the BST thin film was noticed as the most promising material for the capacitor dielectric of future high density DRAM because of high dielectric constant, low leakage current, low temperature coefficient of its electrical properties, small dielectric loss, lack of fatigue or aging problems, and low Curie temperature [1-3]. Although the BST could provide significant potential for improving device performance, simplifying structures and shrinking device sizes, several problems must be overcome for applications to be realized. Among these problems, anisotropic etching of BST thin films is very important in ferroelectric devices to support small feature size and pattern transfer. This is because the barium and strontium contained in BST films are hard to etch. The reason for the difficulty in dry etching BST films is the poor volatility of halogenated compounds of barium and strontium. So, the BST film is more difficult to plasma etch than other high-k materials [4-6].

In this study, inductively coupled plasma etching system was used for BST etching because of its high plasma density, low process pressure and easy control bias power. The dry etching of the BST films was studied using $BCl_3/Cl_2/Ar$ gas chemistry by varying the concentration of the etch gases. Systematic studies were carried out as a function of the etching parameters, including the gas mixture, RF power, working pressure, substrate power, and substrate temperature. The Cl_2/Ar and $BCl_3/Cl_2/Ar$ plasmas were characterized by optical emission spectroscopy (OES) and Langmuir probe.

2. EXPERIMENTAL DETAILS

The BST thin films were deposited by sol-gel method with using alcoxide precursor. The BST films were spin coated at 4000 rpm for 30 s and then dried at 400 ℃ on a hot plate for 10 min to remove organic material. This procedure was performed several times to obtain the final thickness of 200 nm. The pre-baked films were annealed at 700 ℃ for 1 h under an oxygen atmosphere for crystallization.

Etching experiments were performed in planar ICP reactor with the chamber made from aluminum with Al_2O_3 coating of internal walls. A 3.5-turn copper coil, connected to 13.56 MHz power supply, is located above the 24 mm-thick horizontal quartz window. The height of working zone was 9 cm. The bottom electrode used as substrate holder was connected to another 13.56 MHz asymmetric RF generator to control substrate power.

The BST thin films were etched by Cl_2/Ar plasma and adding BCl_3 into $Cl_2(30)/Ar(70)$. The selectivity of BST to the mask material compared to the mask material for BST etching was investigated with varying gas chemistries. Systematic studies were carried out as a function of the etching parameters, including the RF power and substrate power. Etch rates were measured by using a surface profiler (KLA Tencor, alpha-step 500). For these experiments, the total gas flow, process pressure and substrate temperature was 20 sccm, 1.6 Pa, and 20 ℃, respectively The ion current density of the plasma were monitored by a Langmuir probe (HIDEN, ESPION) and the changes of chemical composition in the chamber was analyzed with OES (SC TCEH, PCM 420). We used the software supplied by the equipment manufacturer for obtaining ion current density with the treatment of " voltage-current" traces.

3. RESULTS AND DISCUSSION

BST thin films were etched as a function of the $Cl_2/(Cl_2+Ar)$ and $BCl_3/(Cl_2+Ar)$ ratio. Figure 1 shows the etch rate of the BST thin films and SiO_2 as a function of varying gas chemistries. The total flow rate was 20 sccm, the RF power/substrate power was 700 W/ 300 W, the chamber pressure was 1.6 Pa, and substrate temperature was 20 ℃. As the concentration of $Cl_2/(Cl_2+Ar)$ into gas mixture increases, the etch rate of BST thin films reaches a maximum and then decreases. For $Cl_2/(Cl_2+Ar)$ gas mixing ratio exceeding 0.3, the BST etch rate decreases due to the lower physical bombardment effect by the decrease of Ar concentration in the etching gas. Comparisons of the BST etch rates in Ar only and Cl_2 only plasmas shows that the chemical etching is less effective than physical sputtering. Non-monotonic behavior of the etch rate was obtained in our experiments may be explained as follows. It is well known that all the components of BST film form low-volatile fluorides such as $BaCl_2$ (boiling point: 1560 ℃), $SrCl_2$ (boiling point: 1250 ℃) and $TiCl_4$ (boiling point: 136 ℃). Among them, $BaCl_2$ and $SrCl_2$ are extremely low volatile compounds with a lower boiling point Therefore, we assume that in pure Cl_2 plasma the etch rate is limited by the desorption of the reaction products from the etched surface. Addition of the Ar up to 70% increases the etch rate through the action of two mechanisms: 1) the acceleration chemical reaction owing to the ion-stimulated desorption of reaction products and 2) increasing of the contribution of physical sputtering. Nevertheless, when the Ar content exceeds 70 %, the etch rate begin to fall down to the limit determined by the Ar+ sputtering yield due to "disappearance"of chemical channel. In this case, chemical etching cannot give the noticeable contribution to the etch rate because the volume density of Cl atoms is too low. The etch rate of the BST thin films had a maximum value at 20 % BCl_3 gas concentration and decreased with further addition of BCl_3 gas. The highest BST etch rate was 64.7 nm/min at 20 % BCl_3 added to Cl_2/Ar. It was confirmed in previous research that not only ion bombardment effects but also chemical reactions between the BST film and Cl radicals assists in etching the BST thin films [2, 6].

To understand the roles of physical and chemical effects, the data about the influence of Cl_2 addition on volume densities of active particles and ion current densityare needed. For these purposes we used OES and Langmuir probe analysis. For the control of active species volume densities behavior in Cl_2/Ar and $BCl_3/Cl_2/Ar$ plasmas, we selected such emission maximums as atomic lines of Cl (452.6 nm), Ar (750.4 nm), Cl_2 (307.4 nm), BCl (272 nm), and B (249.6 nm). These maximums are frequently used for analytical purposes including optical emission actinometry to determine absolute densities of active particles. Also, we used the software supplied by the equipment manufacturer for obtaining ion current density with the treatment of " voltage-current" traces.

Figure 1 illustrates variations of emission intensities of selected maximums as a function of Cl_2 and BCl_3 concentration in gas mixtures, respectively. Figure 1 shows that the increasing of Ar content in Cl_2/Ar mixture leads to a direct proportional increase of emission intensity of Ar atoms. The addition of more than 20 % BCl_3 to the Cl_2/Ar chemistry decreased the Cl radical intensity while B radical intensity was increased. The BCl_3 molecule can be dissociated into a B radical and Cl radicals. However, the BCl_3 molecule can be dissociated into a B radical easier than Cl radicals. Therefore, the addition of 30 % BCl_3 into the Cl_2/Ar chemistry decreased the number of Cl radicals because the Ar ion assisted insufficiently in dissociating the molecule into Cl radicals and because there was recombination between the Cl and B species. Therefore, OES data confirm our conclusion that changing of Ar fraction in gas mixtures does not lead to sufficient changes of multiplication of excitation constant and electron density. Analysis of data reported above allows making some conclusions concerning etching mechanism of BST thin films. It is evidently clear that less than two-fold increasing of etching rate in gas mixtures up to 30 % addition of Cl_2 cannot be supported by chemical mechanism because volume densities of chlorine atoms have a tendency to decreasing. To our mind, the increasing

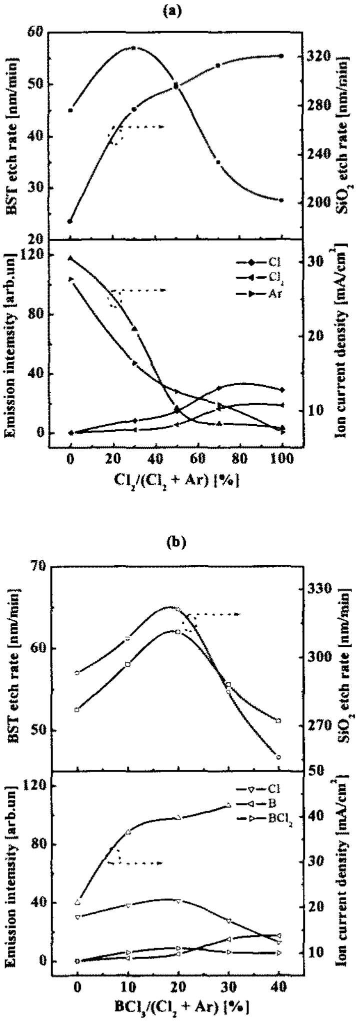

Figure 1. Etch rate of BST and SiO_2, emission intensity, and ion current density as a function of (a) Cl_2/Ar plasma and (b) $BCl_3/Cl_2/Ar$ plasma..

of etch rate may be explained by two factors. First factor is connected with acceleration of physical sputtering of both main material such as PST film and surface layer of reaction products. The evident contribution of physical sputtering in etching process is confirmed by the fact that etching rate in pure Ar is sufficiently more than in Cl_2 gases. Second factor represents the sequence of first one and connected with acceleration of chemical interaction through the increasing of reaction probability and destruction of metal-oxide bonds. As the Ar concentration was decreased, an evident increase of ion current density was observed. Higher ion current density could contribute the higher concentration of reactive species in the plasma and made the etch rate increase. In this case, extreme behavior of etching rate and decreasing of etching rate at Cl_2 content less than 30 % may be connected with decreasing of chemical channel due to rapid decreasing of volume density of chemical active species.

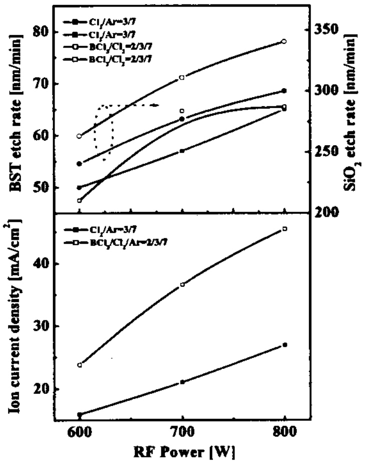

Figure 2. Etch rate of BST and SiO2, and ion current density as a function of RF power.

Figure 2 shows the effect of RF power on the etch rates of BST at a $Cl_2/(Cl_2+Ar)$ of 30 % and $BCl_3/(Cl_2+Ar)$ of 20 %. Other process conditions were equal to Fig. 1. As the RF power increases from 600 to 800 W, the etch rates of BST films increase from 50 to 65 nm/min and from 47.5 to 65.5 nm/min, respectively. It is well known that the increase of RF power results to the increase of both ion density and chlorine atoms density. The improved etching behavior in associated with the enhanced sputtering on the BST surface by increase of ion energy. In Fig 2, ion energy limited regime, it could be that the energy absorbed by surface accelerates etch step [8]. Therefore, in this case, the acceleration of chemical as well as physical etch mechanisms take place simultaneously. That is why we obtained the increase of the etch rate for all the materials were examined.

Figure 3 shows the effect of substrate power varied from 200 to 400 W while keeping RF power and working pressure at 700 W and 1.6 Pa, respectively. The increase of substrate power from 200 to 400 W also linearly increased the BST etch BST thin films were etched with inductively coupled rate from 47 to 68.8 nm/min and from 27.1 to 90.1 nm/min, respectively, as shown in Fig. 3. The influence of the substrate power on the BST etch rate may be explained by the increasing ion bombardment energy and the increasing sputtering yields both for main material and reaction products.

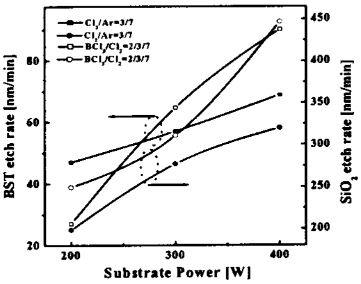

Figure 3. Etch rate of BST and SiO_2 as a function of substrate power.

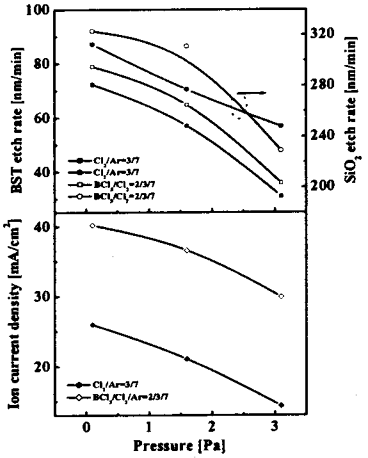

Figure 4. Etch rate of BST and SiO_2, and ion current density as a function of working pressure.

The etch rate as a function of working pressure is shown in Fig. 4. Keeping the RF power, substrate power, and substrate temperature constant at 700 W, 300 W, and 20 ℃, respectively. As the working pressure increase 0.1 to 3.1 Pa, the etch rate of BST and SiO_2 rapidly decreases. Since the mean free paths of species are inversely proportional to pressure, the reduction in potential translates into a lower energy ion flux to the substrate surfaces. That is, high pressures yield lower ion bombardment energies. This correlates well with the pressure effect that the ion bombardment is more effective than chemical etching in the BST etching process.

4. CONCLUSIONS

Cl_2/Ar and $BCl_3/Cl_2/Ar$ plasmas. A chemically assisted physical etch of BST was experimentally confirmed by ICP under various gas mixtures. After a 20 % addition of BCl_3 to the Cl_2/Ar mixture, resulting in an increased the chemical effect. As a increases of

RF power and substrate power, and decrease of working pressure, the ion energy flux and chlorine atoms density increased. The optimum condition appears to be under a 20 % $BCl_3/(Cl_2+Ar)$ gas mixture in the present work. The maximum etch rate of the BST thin films was 90.1 nm/min at the RF power, substrate power, working pressure were 700 W, 300 W, and 1.6 Pa, respectively.

[REFERENCES]

[1] L. Stafford, J. Margot, S. Delprat, M. Chaker, D. Queney, "Sputter-etching characteristics of barium·strontium·titanate and bismuth·strontium·tantalate using a surface-wave high-density plasma reactor", J. Vac. Sci. Technol. A 20, pp. 530~535, 2002.

[2] S. B. Kim, B. J. Min, D. P. Kim, C. I. Kim, "Effects of BCl_3 Addition in Cl_2/Ar Plasma Etching of $(Ba,Sr)TiO_3$ Thin Films", J. Korean Phys. Soc. 38, pp. 264~267, 2001.

[3] S. K. Choi, D. P. Kim, C. I. Kim, and E. G. Chang, "Damage in etching of $(Ba, Sr)TiO_3$ thin films using inductively coupled plasma", J. Vac. Sci. Technol. A 19, pp. 1063~1067, 2001.

[4] D. S. Wuu, C. C. Lin, R. H. Horng, F. C. Liao, Y. H. Liu, "Etching characteristics and plasma-induced damage of high-k $Ba_{0.5}Sr_{0.5}TiO_3$ thin-film capacitors", J. Vac. Sci. Technol. B 19, pp. 2231~2236, 2001.

[5] D. S. Wuu, F. C. Liano, N. H. Kuo, R. H. Horng, M. K. Lee, "Etching Characteristics and Mechanism of $Ba_{0.7}Sr_{0.3}TiO_3$ Thin Films in an Inductively Coupled Plasma", Jpn. J. Appl. Phys. 39, pp. 2068~2072 ,2000.

[6] S. B. Kim, C. I. Kim, E. G. Chang, G. Y. Yeom, "Study on surface reaction of $(Ba, Sr)TiO_3$ thin films by high density plasma etching", J. Vac. Sci. Technol. A 17, pp. 2156~2161, 1999.

[7] Handbook of X-ray Photoelectron Spectroscopy, edited by J. Chastain (Perkin-Elmer, Eden Prairie, NJ, 1992), p. 188.

[8] J. Ding, J. S. Jenq, G. H. Kim, H. L. Maynard, J. S. Hamers, N. Hershkowitz, and J. W. Taylor, "Etching rate characterization of SiO_2 and Si using ion energy flux and atomic fluorine density in a CF_4/O_2/Ar electron cyclotron resonance plasma", J. Vac. Sci. Technol. A 11, pp. 1283~1288, 1993.