Dry Etching of BST using Inductively Coupled Plasma

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BST thin films were etched with inductively coupled $CF_4/(Cl_2+Ar)$ plasmas. The etch characteristics of BST thin films as a function of $CF_4/(Cl_2+Ar)$ gas mixtures were analyzed using optical emission spectroscopy (OES) and Langmuir probe. The BST films in $CF_4/Cl_2/Ar$ plasma is mainly etched by the formation of metal chlorides which depends on the emission intensity of the atomic Cl and the bombarding ion energy. The maximum etch rate of the BST thin films was 53.6 nm/min because small addition of CF_4 to the Cl_2/Ar mixture increased chemical and physical effect. A more fast etch rate of BST films can be obtained by increasing the DC bias and the RF power, and lowering the working pressure.

Keywords : ICP, Etching, BST, OES, Langmuir probe

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[1-4]. 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, because the barium and strontium contained in BST films are hard to be etched. 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[5-7].

In this study, the 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 $CF_4/Cl_2/Ar$ gas chemistry by varying the concentration of the etch gases. Systematic studies were carried out as a function of the RF power and the DC bias voltage to the substrate. The changes of chemical composition in the chamber were analyzed with 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 °C 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 °C for 1 h under an oxygen atmosphere for crystallization.

Experiments were carried out in planar ICP reactor, which is schematically shown in Fig. 1 and the etching conditions are summarized in Table 1. The reactor consists of cylindrical aluminum anodized chamber with diameter of 26 cm. One vertical view port on the chamber wall-side provides the installation of diagnostics tools such as OES and Langmuir probe. A 3.5-turn copper coil, connected to 13.56 MHz power generator, is located above the 24 mm-thick horizontal quartz window.

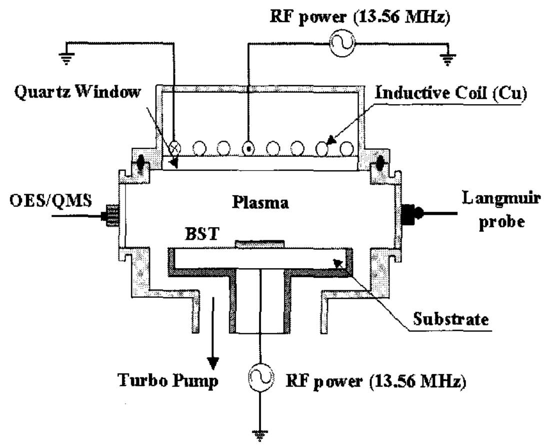

Fig. 1. Schematic diagram of ICP reactor.

The height of working zone, i.e. the distance between horizontal quartz window and bottom electrode, was 9 cm. The bottom electrode was connected to another 13.56 MHz asymmetric RF generator to control dc bias voltage.

The BST thin films were etched by adding CF_4 into $Cl_2(20)/Ar(80)$. Systematic studies were carried out as a function of the etching parameters, including the DC bias voltage to the substrate. Etch rates were measured by using a surface profiler (Tencor, α-step 500). Plasma emission spectra were measured using the grating monochromator (SC TCEH, PCM 420). The primary measured emission intensities were corrected taking into account the non-linear spectral characteristic of optical sensor. Langmuir probe measurements were performed by the single, cylindrical, rf-compensated probe (ESPION, Hiden Analytical), placed in the center of reactor working zone both in axial and radial positions. For the treatment of "voltage-current" characteristics aimed to obtain electron temperature and ion current density, we used the software applied by the equipment manufacturer.

Table 1. ICP etching conditions of BST films.

Etch parameters	Etch conditions (standard condition)
Etch gas	$CF_4/Cl_2/Ar$
Total flow rate	20 sccm
RF power	600 – 800 W (700 W)
DC bias	-100 – -200 V (-150 V)
Working pressure	2 – 6 Pa (2 Pa)
Substrate temperature	25 °C

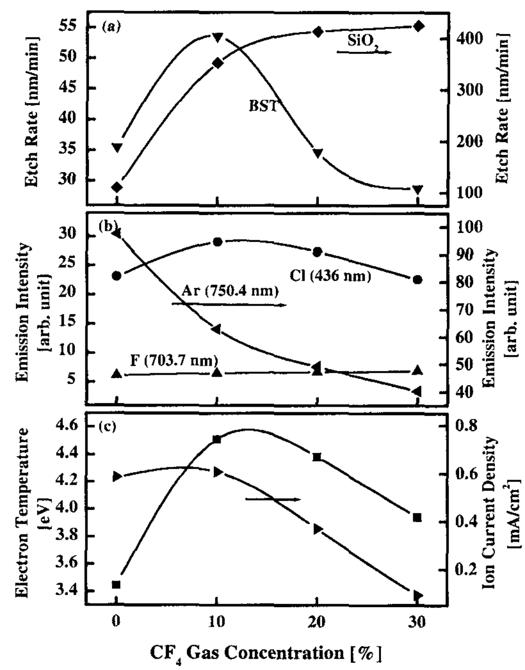

Fig. 2. (a) Etch rate of BST and SiO_2, (b) emission intensities of Cl (436 nm), F (703.7 nm) and Ar (750.4 nm), (c) electron temperature and ion current density in Cl-based ICP plasma as a function of additive gas percentage.

3. RESULTS AND DISCUSSION

BST thin films were etched as a function of the $CF_4/(Cl_2+Ar)$ ratio. Figure 2 shows the etch rate of the BST thin films and SiO_2 at varying concentrations of CF_4 gas. The $Cl_2/(Cl_2+Ar)$ ratio was fixed at 0.2 in this experiment to give the optimal Cl_2/Ar gas mixing ratio determined in previous study[2]. The standard conditions listed in Table 1 were used as etching conditions, unless otherwise specified. The etch rate of the BST thin films had a maximum value at 10 % CF_4 gas concentration and decreased with further addition of CF_4 gas because BaF_X and SrF_X compounds have a higher melting and boiling points than $BaCl_X$ and $SrCl_X$[8]. The highest BST etch rate was 53.6 nm/min at 10 % CF_4 added to Cl_2/Ar plasma. 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. As the amount of added gas (CF_4) was increased, the etch rate of SiO_2 increased, and the selectivity of the BST to SiO_2 decreased. The etch rates of SiO_2 was greatly changed because the F radicals effect the etching of SiO_2.

To understand the effect of the additional CF_4 gas into Cl_2/Ar plasma on the BST etch rates, the characteristics of $CF_4/Cl_2/Ar$ plasmas were investigated using OES and Langmuir probe, and the results are shown in Fig. 2. For the control of radical volume densities behavior in $CF_4/$

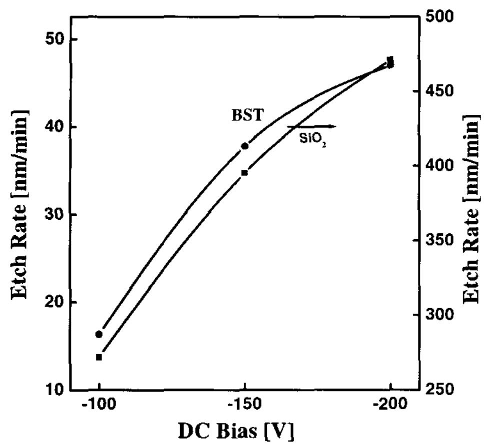

Fig. 3. Etch rate of BST and SiO_2 in Cl-based ICP plasma as a function of the DC bias.

Cl_2/Ar plasmas, we estimated the Ar (750.4 nm) ion, Cl (436 nm) and F (703.7 nm) radical densities using OES. Figure 2 shows the optical emission intensity of various species, the electron temperature and the ion current density as a function of additive CF_4 gas concentration in fixed Cl_2/Ar gas mixing ratio of 8/2. As the CF_4 gas concentration increases, the optical emission intensity of the F radical is increases while the optical emission intensity of Ar ion decreases. The optical emission intensities of the Cl radicals, the electron temperature and the ion current density have a maximum value at 10 % CF_4 concentration, as does the BST etch rate. As the gas mixing ratio increases to 10 % CF_4, the electron temperature increases. Actually, electron temperature increases from 3.4 eV up to 4.5 eV. Those bring about the increase of electron-molecule reactions. Electron-molecule reactions are responsible for ionization and dissociation in the plasma[9]. The BST etch rate is strongly dependent on Cl radical concentration rather than F radical concentration because of the higher vapor pressure of metal chlorides compared to metal fluorides. However, BST etch rate had a maximum value at 10 % CF_4 because TiFx compounds have a lower melting point and boiling point than TiClx.

The behaviors of etch rates and analyses of OES and Langmuir probe allow us making some conclusions concerning etching mechanism of BST thin films. In this situation, the increasing of etch rate may be explained by two factors. First factor is connected with acceleration of physical sputtering of both main material such as BST film and surface layer of reaction products. Second factor represents the sequence of first one and connected with acceleration of chemical interaction through the increase of reaction probability and destruction of metal-oxide bonds.

Figure 3 shows the effect of DC bias voltage varied

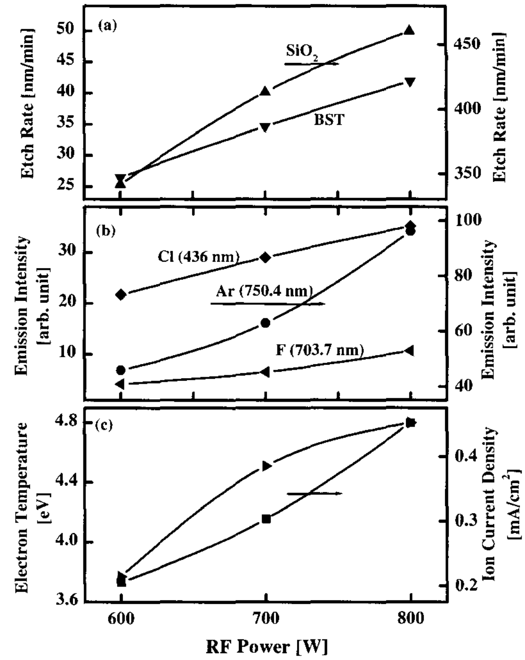

Fig. 4. (a) Etch rate of BST and SiO_2, (b) emission intensities of Cl (436 nm), F (703.7 nm) and Ar (750.4 nm), (c) electron temperature and ion current density in Cl-based ICP plasma as a function of the RF power.

From –100 to –200 V. The increase of DC bias voltage from –100 to –200 V also linearly increased the BST etch rate from 13.7 to 47.6 nm/min, as shown in Fig. 3. The influence of the DC bias voltage on the BST etch rate may be explained by the increasing ion bombardment energy and the increasing sputtering yields for both main material and reaction products. The etch selectivity of BST to SiO_2 appears to be increased slightly with the increase of DC bias voltage, suggesting lower sensitivity of SiO_2 etching on the ion bombardment.

Figure 4 shows the effect of coil RF power on the etch rates of BST, the optical emission intensity of various species, the electron temperature and the ion current density under 20 % CF_4 in a Cl_2/Ar gas mixture. As the coil RF power increases from 600 to 800 W, the etch rates of BST films, the optical emission intensity of various species, the electron temperature and the ion current density increases. As the coil RF power increases the plasma density increases and the molecules are dissociated more effectively, thus producing more radicals and ions[10]. Therefore, in this case, the acceleration of chemical as well as physical etch mechanisms takes place simultaneously. That is why we obtained the increase of the etch rate for all the materials were examined.

Figure 5 shows the dependence of the BST and SiO_2 etch rate, the optical emission intensity of various species

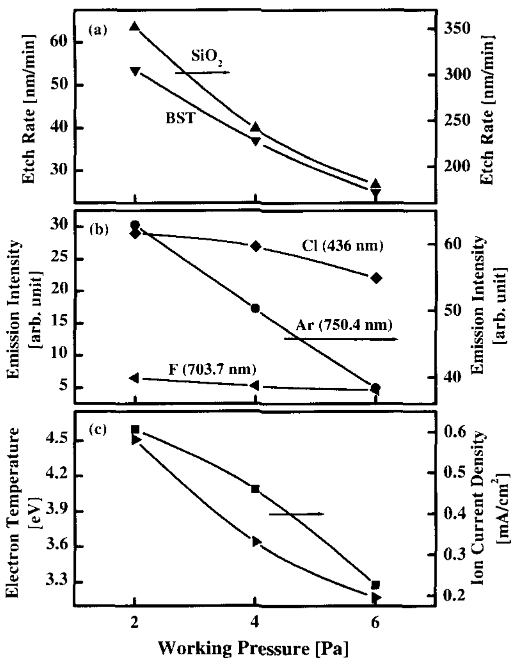

Fig. 5. (a) Etch rate of BST and SiO_2, (b) emission intensities of Cl (436 nm), F (703.7 nm) and Ar (750.4 nm), (c) electron temperature and ion current density in Cl-based ICP plasma as a function of the working pressure.

the electron temperature and the ion current density on the working pressure in 10 % CF_4 in a Cl_2/Ar plasma. As the working pressure increase 2 to 6 Pa, the etch rate of BST and SiO_2, the optical emission intensity of various species, the electron temperature and the ion current density rapidly decreases. As the working pressure is lowered, the characteristic potentials across the sheaths and the voltage applied to a discharge increase sharply. As bias is proportional to the peak applied voltage, it rises too. Since the mean free paths of species are inversely proportional to pressure, the rise in potential translates into a higher energy ion flux to substrate surfaces. Sputtering does not take place until ion bombardment energy exceeds a material and ion specific threshold[11], at which point sputtering rates increase rapidly as ion energies move above the threshold. 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

In this study, BST thin films were etched with inductively coupled CF_4/(Cl_2+Ar) plasmas. A chemically assisted physical etch of BST was experimentally confirmed by ICP under various gas mixtures. The etch rate of the BST thin films had a maximum value at 10 % CF_4 gas concentration and decreased with further addition of CF_4 gas because BaF_X and SrF_X compounds have a higher melting and boiling points than $BaCl_X$ and $SrCl_X$. The maximum etch rate of the BST thin films was 53.6 nm/min because small addition of CF_4 to the Cl_2/Ar mixture increased chemical and physical effect. The characteristics of the plasma were analyzed using OES and Langmuir probe. The optimum condition appears to be under a 10 % CF_4/(Cl_2+Ar) gas mixture in the present work. A more fast etch rate of BST films can be obtained by increasing the DC bias and the RF power, and lowering the working pressure.

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