유도결합 플라즈마를 이용한 BST 박막의 식각 특성 연구

김관하, 김경태, 김창일*, 김태형**, 이철인***
중앙대학교*, 여주대학**, 안산공과대학***

A study on the etch characteristics of BST thin films using inductively coupled plasma

Gwan-Ha Kim, Kyoung-Tae Kim, Chang-Il Kim*, Tae-Hyung Kim**, Chul-In Lee***
ChungAng Uni.*, Ansan College of Technology**, YeoJoo Institute of Technology***

Abstract

In this study, 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 quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES). 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 effect. The optimum condition appears to be under a 10 % $CF_4/(Cl_2+Ar)$ gas mixture in the present work.

Key Words : Etching, BST, ICP, QMS, OES)

I. Introduction

With the increasing density of memory devices, ferroelectric thin films that possess ahigh 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, lowleakage current, low temperature coefficient of its electrical properties, small dielectric loss, lack of fatigue or aging problems, and low Curie temperature [1-2]. 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 [3,4].

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 was analyzed with quadrupolemass spectrometry (QMS) and optical emission spectroscopy (OES).

II. EXPERIMENTAL DETAILS

The BST thin films were deposited by sol-gel method. Experiments were carried out in planar ICP reactor.

The BST thin films were etched by adding CF_4 into $Cl_2(20)/Ar(80)$. The selectivityof BST compared to the mask material for BST etching was investigated with varying $CF_4/(Cl_2+Ar)$ gas mixing ratio. 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, -step 500). For these experiments, the total gas flow and process pressure was 20 sccm and 2 Pa, respectively. To investigate the characteristics of the plasmas more closely, the ralative amounts of neutral species were estimated by quadrupole mass spectrometry (QMS: Hiden Analytical Inc. HAL 510). The mass resolution of the QMS system used in this experiment was 0.01 amu. Plasma emission spectra were measured using the optical emission spectroscopy (OES: SC TCEH, PCM 420). The primary measured emission intensities were corrected taking into account the non-linear spectral characteristic of optical sensor.

III. Results and Discussion

BST thin films were etched as a function of the $CF_4/(Cl_2+Ar)$ ratio. Figure 1 shows the etch rate of the BST thin films and selectivity of BST to 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 Cl_2/Ar flow rate was 20 sccm, the RF power/DC bias were 700 W/ -150 V, and the chamber pressure was 2 Pa. 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 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_2decreased. The etch rates of SiO_2 was greatly changed because the F radicals effect the etching of SiO_2.

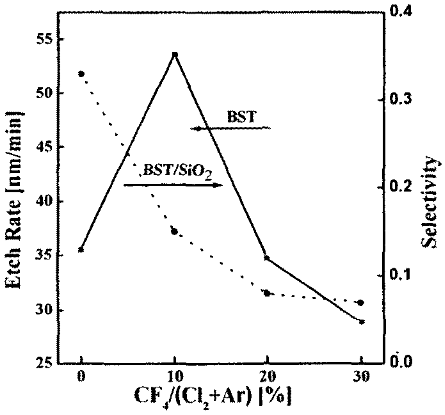

Figure 1. Etch rate of BST and selectivity of BST to SiO_2 in Cl-based ICP plasma as a function of additive gas percentage.

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

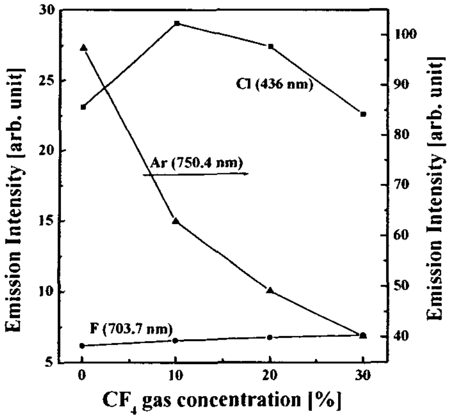

Figure 2. Emission intensities of Cl (436 nm), F (703.7 nm)and Ar (750.4 nm) in Cl-based ICP plasma as a function of additive gas percentage.

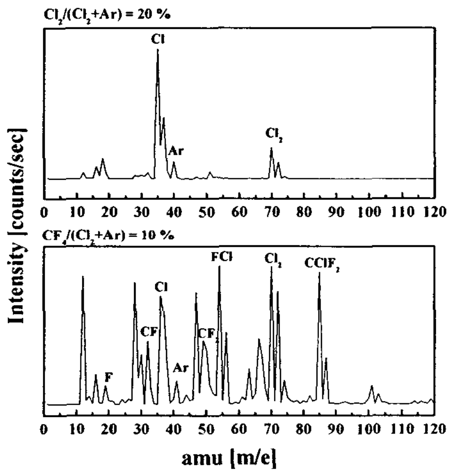

Figure 3. The mass scan results of positive ions obtained by QMS in various etching condition.

investigated using QMS and OES, and the results are shown in Fig. 2 for OES and Fig. 3 for QMS. For the control of radical volume densities behavior in $CF_4/Cl_2/Ar$ plasmas, we estimated the Ar (750.4nm) ion, Cl (436nm) and F (703.7nm) radical densities using OES. Figure 3 shows the optical emission intensity of various species 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, theoptical emission intensity of F radical is increases while the optical emission intensity of Ar ion decreases. The Cl optical emission intensity increase rapidly as the CF_4 gas concentration increases. The optical emission intensities of the Cl radicals have a maximum value at 10% CF_4 concentration, as does the BST etch rate. 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. When the radicals from $CF_4/Cl_2/Ar$ plasmas were measured using QMS, the peaks from F, Cl, FCl, CF, CF_2, and $CClF_2$ were observed. From the OES and the QMS results, the addition of small amount of CF_4 to Cl_2 enhances the generation of atomic Cl by the reactions of Eqs. (1a) and (1b).

$$Cl_2 + F \rightarrow FCl + Cl \qquad (1a)$$

$$Cl_2 + CF_2 \rightarrow CClF_2 + Cl \qquad (1b)$$

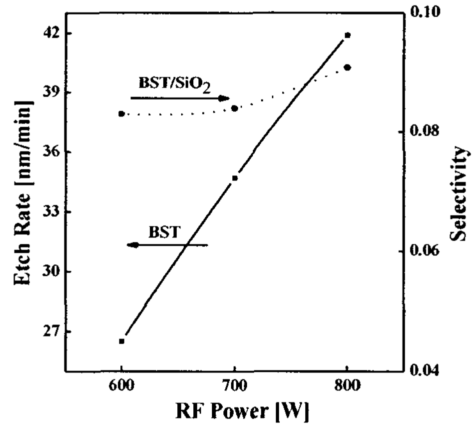

Figure4. Etch rate of BST and selectivity of BST to SiO_2 as a function of the RF power.

Figure 4 shows the effect of coil RF power on the etch rates of BST under 20% CF_4 in a Cl_2/Ar gas mixture. Other process conditions were equal to Fig.1. As the coil RF power increases from 600 to 800 W, the etch rates of BST films increase from 26.5 to 41.9 nm/min. Meanwhile, as shown in Fig. 5, the etch selectivity of BST to

SiO_2 remained similar regardless of inductive power. It is well known that the increase of coil RF power results inthe increase of both ion density and fluorine atoms density. 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.

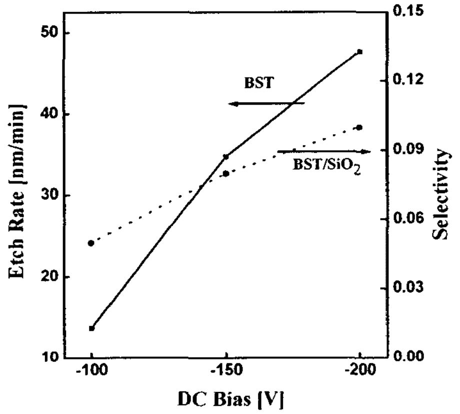

Figure5. Etch rate of BST and selectivity of BST to SiO_2 as a function of the DC bias.

Figure 5 shows the effect of DC bias voltage varied from 100 to 200 V while keeping the CF_4 in a Cl_2/Ar gas mixture, inductive power, and operational pressure at 20% CF_4, 700 W, and 2 Pa, respectively. 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. 5. 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 tobe increased slightly with the increase of DC bias voltage, suggesting lower sensitivity of SiO_2 etching on the ion bombardment.

Ⅳ.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 effect. The characteristics of the plasma were analyzed using OES and QMS. The optimum condition appears to be under a 10 % CF_4/(Cl_2+ Ar) gas mixture in the present work.

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