한국전기전자재료학회 2004년도 하계학술대회 논문집

초고주파 응용을 위한 BST 박막의 식각 특성

김관하, 김창일
중앙대학교

Etching characteristics of BST thin films for microwave application

Gwan-Ha Kim, Chang-Il Kim*
Chung-Ang University

Abstract

BST thin films were etched with inductively coupled $CF_4/(Cl_2+Ar)$ plasmas. The maximum etch rate of the BST thin films was 53.6 nm/min for a 10 % CF_4 to the Cl_2/Ar gas mixture at RF power of 700 W, DC bias of -150 V, and chamber pressure of 2 Pa. Small addition of CF_4 to the Cl_2/Ar mixture increased chemical effect. Consequently, the increased chemical effect caused the increase in the etch rate of the BST thin films. To clarify the etching mechanism, the surface reaction of the BST thin films was investigated by X-ray photoelectron spectroscopy.

Key Words : inductively coupled plasma, BST thin films, etching, XPS

1. Introduction

Recently, there is a great interest in the application of ferroelectric and paraelectric thin films for tunable microwave device such as electricallytunable mixers, delay line, filters, capacitor, oscillators, resonators and phase shifters.. Ferroelectric materials are characterized by sufficient advantages including the possibility of dielectric constant adjustment by the electric field applied. For microwave 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 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, 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 [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 $CF_4/Cl_2/Ar$ gas chemistry by varying the concentration of the etch gases.

2. Experimental Details

Etching experiments were performed in planar ICP reactor with the chamber made from stainless steel with Al_2O_3 coating of internal walls.

The BST thin films were etched by adding CF_4 into $Cl_2(20)/Ar(80)$. The selectivity of BST compared to the mask material for BST etching was investigated with varying $CF_4/(Cl_2+Ar)$ mixing ratio. Systematic studies were carried out as a function of the etching parameters, including the RF power and 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 sccmand 2 Pa, respectively. For the study of chemical reaction on the etched surface, the surfaces of BST films etched with different $CF_4/Cl_2/Ar$ gas mixing ratios were investigated using XPS (ESCALAB 250).

3. 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 PST thin films had a maximum value at 10 % CF_4 gas concentration and decreased with further addition of CF_4 gas. The highest BST etch rate was 53.6 nm/min at 10 % CF_4 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]. As the amount of added gas (CF_4) was increased, the etch rate of SiO_2increased, 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.

Figure 2 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. 2, the etch selectivity of BST to SiO_2 remained similar regardless of inductive power.

Figure 3 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. 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 chemical reactions between the elementsof BST (Ba, Sr, Ti, O) and radicals (Cl and F) were investigated by using XPS narrow scan spectroscopy. All the samples used were bare BST films without any photoresist treatment. Gas mixing ratio is 20 % CF_4 in a Cl_2/Ar gas mixture. The variations of the Ba, Sr, Ti, and O peaks of the etched BST surfaces are shown in from Fig. 4 to Fig. 6. for a 20 % CF_4 in the Cl_2/Ar gas mixing ratio. Figure 4 shows that the Ba 3d spectra can be resolved as BaO, $BaCl_2$, and BaF_2. The Ba 3d peaks at 779.1 eV, 781.7 eV, and 779.8 eV binding energies correspond to BaO, $BaCl_2$, and BaF_2, respectively [7]. Spectrum (2) in Fig. 4 shows that the intensities of the BaO and the $BaCl_2$peaks are lower than the intensities of the other peaks. And spectrum (1) in Fig. 4 shows that the intensities of the Ba and the BaO peaks are higher than the intensities of the other peaks. It reveals that Ba is removed by chemical reactions with Cl and F radicals and by physical bombardment of Ar ions.

Figure 5 shows that the Sr 3d spectra can be resolved into Sr, SrO, $SrCl_2$, and SrF_2. Spectrum (2) in Fig. 5 shows that Ba-Ti-O and Sr-Ti-O bonds are broken on the BST surface during the etch, so Ba and Ti atoms can be removed with ease, but Sr atoms were hard to remove because byproducts (such as $SrCl_2$, SrF_2) are nonvolatile. Therefore, it can be confirmed that there are chemical reactions between F and Sr.

The Ti 2p spectra are shown in Fig. 6. Spectrum (2) in Fig. 6 shows that Ti is removed almost completely by chemical reaction (such as $TiCl_4$) because chlorinated compounds are volatile. Based on these results, simultaneous physical enhancement and chemical reaction will be required to etch the BST efficiently.

4. Conclusion

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 optimum condition appears to be under a 10 % $CF_4/(Cl_2+Ar)$ gas mixture in the present work. The maximum etch rate of the BST thin films was 53.6 nm/min. Small addition of CF_4 to the Cl_2/Ar mixture increased chemical effect. Consequently, the increased chemical effect caused the increase in the etch rate of the BST thin films. Based on the XPS, Ba, Sr, and Ti exhibit different etching effects in the ICP process. It is necessary to study how Sr can be removed effectively because $SrCl_2$ and SrF_2 are nonvolatile.

References

[1] L. Stafford, J. Margot, S. Delprat, M. Chaker, D. Queney, J. Vac. Sci. Technol. A 20 (2002) 530.

[2] S. B. Kim, B. J. Min, D. P. Kim, C. I. Kim, J. Korean Phys. Soc. 38 (2001) 264.

[3] S. K. Choi, D. P. Kim, C. I. Kim, and E. G. Chang, J. Vac. Sci. Technol. A 19 (2001) 1063.

[4] D. S. Wuu, C. C. Lin, R. H. Horng, F. C. Liao, Y. H. Liu, J. Vac. Sci. Technol. B 19 (2001) 2231.

[5] D. S. Wuu, F. C. Liano, N. H. Kuo, R. H. Horng, M. K. Lee, Jpn. J. Appl. Phys. 39 (2000) 2068.

[6] S. B. Kim, C. I. Kim, E. G. Chang, G. Y. Yeom, J. Vac. Sci. Technol. A 17 (1999) 2156.

[7] David R. Lide , CRC handbook of chemistry and physics, CRC Press LLC, Washington D.C., 1998, p. 4-66.

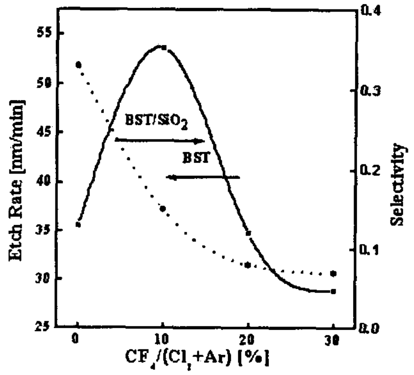

Fig. 1. Etch rate of BST and selectivity of BST to SiO_2 as a function of the addition of CF_4 to Cl_2/Ar gas.

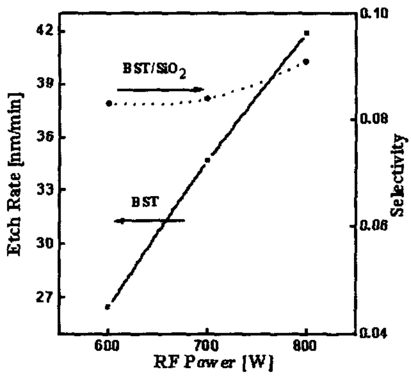

Fig. 2. Etch rate of BST and selectivity of BST to SiO_2 as a function of the RF power.

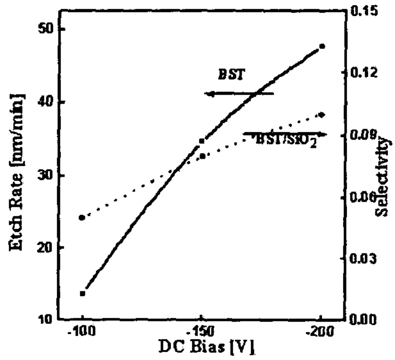

Fig. 3. Etch rate of BST and selectivity of BST to SiO_2 as a function of the DC bias.

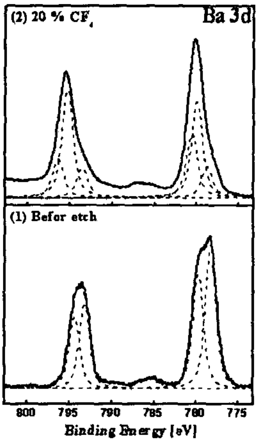

Fig. 4. Ba 3d XPS narrow scan spectra of the BST surface etched under a $CF_4/(Cl_2+Ar)$ gas mixture.

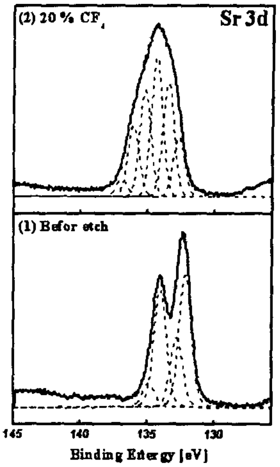

Fig. 5. Sr 3d XPS narrow scan spectra of the BST surface etched under a $CF_4/(Cl_2+Ar)$ gas mixture.

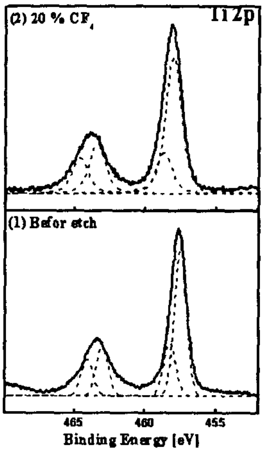

Fig. 6. Ti 2p XPS narrow scan spectra of the BST surface etched under a $CF_4/(Cl_2+Ar)$ gas mixture.