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유도결합플라즈마를 이용한 BST 박막의 건식 식각 특성

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Dry etching of BST thin films using inductively coupled plasma

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Abstract - In this work, we investigated etching characteristics and mechanism of BST thin films using Cl_2/Ar, $CF_4/Cl_2/Ar$ and $BCl_3/Cl_2/Ar$ gas mixtures using inductively coupled plasma (ICP) system. 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 20 % $BCl_3$and 10 % CF_4 gas concentration, and decreased with further addition of BCl_3 or CF_4 gas, because $BaCl_x$, $SrCl_x$, BaF_x and SrF_x compounds have higher melting and boiling points. The maximum etch rate of the BST thin films was 57 nm/min at the 30 % $Cl_2/(Cl_2+Ar)$.The characteristics of the plasma were analyzed by using OES and 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 [1-3]. 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 work, we investigated etching characteristics and mechanism of BST thin films using Cl_2/Ar, $CF_4/Cl_2/Ar$ and $BCl_3/Cl_2/Ar$ gas mixtures using inductivelycoupled plasma (ICP) system. Etching characteristics were investigated in the terms of BST etch rate and selectivity over photoresist (PR) mask as a function of gas mixing ratio. Plasma diagnostics were performed by Langmuir probe and optical emission spectroscopy (OES) measurements.

2. Experimental Details

The BST thin films were deposited by sol-gel method by using alcoxide precursor. The BST films were spin coated at 4000 rpm for 30 s and then dried at 400C on a hot plate for 10 min to remove organic material. This procedure was performed several times to obtain the final thickness of 3000 Å. The pre-baked films were annealed at 650 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. 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 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. 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 Cl_2/Ar mixture was employed as enchants. Electronic grade gases comprising these mixtures were injected into the ICP source through mass flow controllers at a total flow rate of 20 sccm for Cl_2/Ar.

Plasma diagnostics was performed by Langmuir probe (LP) and optical emission spectroscopy (OES). The installation of diagnostic tools was provided through the vertical view port on the chamber wall-side. LP measurements were carried out using single, cylindrical, and rf-compensated probe (ESPION, Hiden Analytical). The probe was placed at 3 cm above the bottom electrode and centered in radial position. For the treatment of "voltage-current" traces aimed to obtain electron temperature and electron density, we used the software applied by equipment manufacturer. OES measurements were carried out using the grating monochromator (NTS-U101, Nanotek) with the wavelength scope of 200-800 nm.

3. Results and Discussion

For any plasma etch process with using a chemical active gas, there are two general factors affected the behavior of etch rate. The first is the fluxes of active species on the etched surface. The fluxes depend on stationary mass composition of gas phase resulted from the balance between formation and decay processes. Second factor works through the reaction probability and sputtering yields for main material as well as for low-volatile reaction products. Therefore, the investigations of etch mechanism is a complex task, which includes the simultaneous analysis of both volume and surface kinetics.

BST thin films were etched as a function of the $Cl_2/(Cl_2+Ar)$, $BCl_3/(Cl_2+Ar)$ and $CF_4/(Cl_2+Ar)$ratio. Figure 2 shows the etch rate of the BST thin films and the selectivity BST to 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 C. 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 theetching 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 chlorides 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_2plasma 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) theacceleration 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 trend of Fig. 3 is similar to that of Fig. 2. The etch rate of the BST thin films had a maximum value at 20 % BCl_3 gas concentration and decreasedwith 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].

Figure 4 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. The Cl_2/Ar flow rate was 20 sccm, the RF power/DC bias was 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_xcompounds have higher melting and boiling points than $BaCl_x$ and $SrCl_x$ [7]. 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 assist in etching the BST thin films. 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 were greatly changed because the F radicals effect the etching of SiO_2.

Figure 5 and 6illustrates variations of emission intensities of selected maximums as a function of Cl_2 and BCl_3 concentration in gas mixtures, respectively. Figure 5 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_3molecule can be dissociated into a B radical and Cl radicals. However, the BCl_3molecule 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 lessthan two-fold increasing of etching rate in gas mixtures up to 30 % addition of Cl_2cannot be supported by chemical mechanism because volume densities of chlorine atoms have a tendency to decreasing. To our mind, the increasing of etching 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. 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 factorrepresents 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_2content less than 30 % may be connected with decreasing of chemical channel due to rapid decreasing of volume density of chemical active species.

To understand the effect of the additional CF_4 gas added to Cl_2/Ar plasma on the BST etch rates, the characteristics of $CF_4/Cl_2/Ar$ plasmas were investigated by using OES, and the results are shown in Figure 7. For the control of radical volume densities behavior in $CF_4/Cl_2/Ar$ plasmas, we estimated the Ar (750.4 nm) ion, Cl (436 nm) and F (703.7 nm) radical densities by using OES. Figure 7 shows the optical emission intensity of various species as a function of additive CF_4 gas concentration at a fixed Cl_2/Ar gas mixing ratio of 2/8. As the CF_4gas concentration increases, the optical emission intensity of F radical increases, while the optical emission intensity of Ar ion decreases. The Cl optical emission intensity increases rapidly as the CF_4 gas concentration increases. The optical emission intensities of the Cl radicals have a maximum value at 10% CF_4concentration, 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 metalchlorides compared to metal fluorides.

3. Conclusiion

In this study, BST thin films were etched with inductively coupled Cl_2/Ar, $BCl_3/(Cl_2+Ar)$ and $CF_4/(Cl_2+Ar)$ 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 20 % BCl_3 and 10 % CF_4 gas concentration, and decreasedwith further addition of BCl_3 or CF_4 gas, because $BaCl_x$, $SrCl_x$, BaF_x and SrF_x compounds have higher melting and boiling points. The maximum etch rate of the BST thin films was 57 nm/min at the 30 % $Cl_2/(Cl_2+Ar)$. 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.

[Reference]

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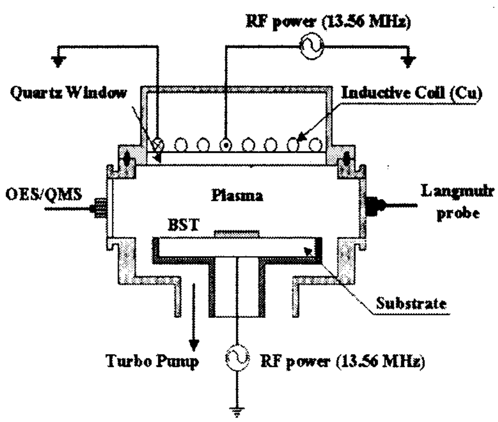

Figure1.Aschematicviewoftheexperimentalsetup.

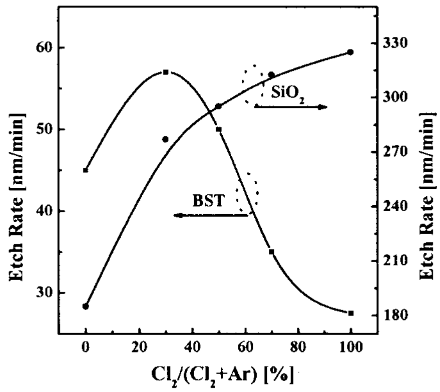

Figure2.EtchrateofBSTthinfilmandselectivityofBSTtoSiO_2inCl-basedICPplasmaasafunctionofCl_2/Argasmixingratio.

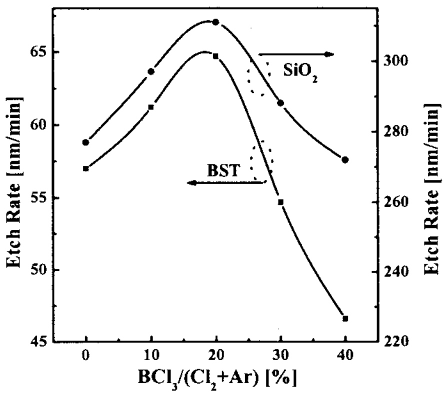

Figure3.EtchrateofBSTthinfilmandSiO_2inCl-basedICPplasmaasafunctionofBCl_3additivegaspercentage.

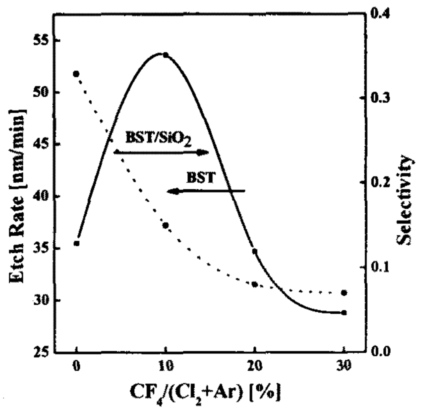

Figure4.EtchrateofBSTthinfilmandselectivityofBS TtoSiO$_2$inCl-basedICPplasmaasafunctionofCF$_4$addi tivegaspercentage.

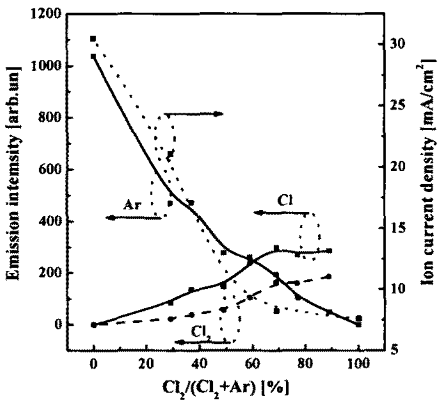

Figure5.EmissionintensitiesofCl(436nm),Cl$_2$(307.4n m)andAr(750.4nm),andioncurrentdensityinCl-based ICPplasmaasafunctionofCl$_2$/Argasmixingratio.

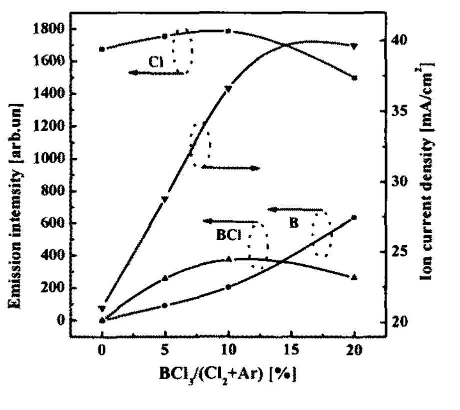

Figure6.EmissionintensitiesofCl(436nm),Cl$_2$(307.4n m),BCl(272nm),B(249.6nm)andAr(750.4nm),andion currentdensityinCl-basedICPplasmaasafunctionofa dditivegaspercentage.

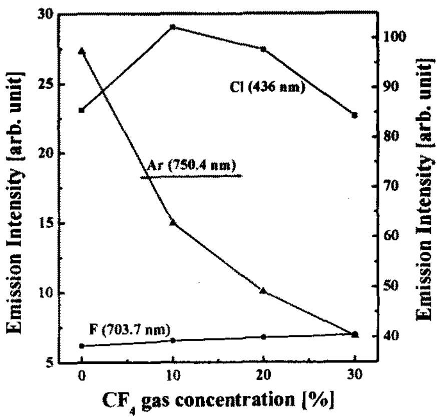

Figure7.EmissionintensitiesofCl(436nm),F(703.7n m)andAr(750.4nm)inCl-basedICPplasmaasafunctio nofCF$_4$additivegaspercentage.