

유도결합 플라즈마를 이용한 BST 박막의 식각 특성 및 모델링

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Etching characteristics and modeling of BST thin films using inductively coupled plasma

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Abstract

This work was devoted to an investigation of etching mechanisms for (Ba,Sr)TiO₃ (BST) thin films in inductively coupled CF₄/Ar plasma. We have found that an increase of the Ar content in CF₄/Ar plasma causes non-monotonic behavior of BST etch rate, which reaches a maximum value of 40 nm/min at 80% Ar. Langmuir probe measurements show a weak sensitivity of both electron temperature and electron density to the change of CF₄/Ar mixing ratio. 0-D model for plasma chemistry gave monotonic changes of both volume densities and fluxes for active species responsible for the etching process. The analysis of surface kinetics confirms the possibility of non-monotonic etch rate behavior due to the concurrence of physical and chemical pathways in ion-assisted chemical reaction.

Key Words : BST, Etch rate, Electron temperature, Ion-assisted etching

I. 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)O₃ (PZT), (Ba,Sr)TiO₃ (BST), SrBi₂Ta₂O₉ (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 CF₄/Ar gas mixtures in an inductive coupled plasma (ICP) system. Etching characteristics were investigated in the terms of BST etch rate and selectivity over photoresist (PR) mask as a function of CF₄/Ar mixing ratio. Plasma diagnostics were performed by Langmuir probe measurements. To understand the etching mechanism, the models of plasma chemistry and surface kinetics were developed.

II. EXPERIMENTAL DETAILS

(Ba,Sr)TiO₃ thin films were prepared according to a formula of Ba_{0.6}Sr_{0.4}TiO₃ using sol-gel method. Experiments were carried out in a planar ICP reactor, which is described in details in our earlier works [7]. Plasma diagnostics was represented by Langmuir probe (LP) measurements. For this purpose, we used a single cylindrical, and rf-compensated probe (ESPION, Hiden Analytical), which was installed through vertical view port on the chamber wall-side and placed in the center of the reactor working zone both in axial and radial directions. For the treatment of "voltage-current" traces aimed at obtaining electron temperature and electron density, we used software supplied by the equipment manufacturer.

III. RESULTS AND DISCUSSION

Figure 1 illustrates the effect of CF₄/Ar mixing ratio on the etch rate of BST thin films as well as on the etch selectivity of BST over PR. Data show that the BST etch rate is non-monotonic and exhibits a maximum at 80% Ar. The absolute value of the etch rate at the maximum is about 40 nm/min. The lowest etch rate was obtained in our experiments corresponds to a pure CF₄ plasma (22 nm/min) while the etching in pure Ar plasma is about 1.5 times faster (32 nm/min). Experiments show also that any variations of input power and

negative dc bias voltage in the range of 600 800 W and 150 250 V do not influence the shape of the curve shown in Fig.1, but result in changes of absolute value for BST etch rate as well as in weak deviations of the position of etch rate maximum along the x-axis. For the PR, an increase of Ar content in CF₄/Ar mixture leads to monotonic decrease in the PR etch rate in the range of 0.96 0.74 m/min. As a result, the etch selectivity of BST over PR follows the behavior of BST etch and enriches a maximum of 0.049 for 80% Ar.

Figure 2 illustrates the results of plasma diagnostics using Langmuir probes. It can be seen that the influence of CF₄/Ar mixing ratio both on electron temperature and electron density is not very significant. Actually, as the Ar content in CF₄/Ar plasma increases from 0 to 100%, electron temperature drops down from 6.5 to 5.9 eV while electron density increases in the range of 5.35 X 10¹⁰ - 8.80 X 10¹⁰ cm⁻³. An only weak change of electron temperature mentioned in experiments is caused by rather close values of ionization potentials for CF₄ and Ar: 15.9 and 15.8 eV, respectively.

To investigate the relationships between composition of gas phase and surface kinetics, we used the phenomenological model based on theory of active surface sites [8]. The model was based on such assumptions as: 1) only F atoms are effective in chemical reaction; 2) only Ar⁺ ions are effective in the sputtering process; 3) sputtering of the substrate is possible only when the incident ion impacts the clean surface 4) all kinds of positive ions are effective for the ion-stimulated desorption of reaction products.

Total etching rate obtained in experiments may be represented as the sum of partial rates of chemical reaction and physical sputtering:

$$ER = (1 - \Theta) \gamma_{ch} S_F \Gamma_F + (1 - \Theta) Y_s \Gamma_{Ar^+} \quad (1)$$

where Γ - fluxes of species to the etched surface, Y_s - sputtering yield, γ_{ch} - probability of chemical interaction, S_F - sticking probability of

F atoms, Θ - fraction of fluorinated surface. Assuming the contribution of spontaneous chemical etching to be negligible, stationary balance equation for active sites on the surface may be written as follows:

$$(1-\Theta)\gamma_{ch}S_F\Gamma_F = \Theta\sum Y_{d,j}\Gamma_{+,j} \quad (2)$$

where Y_{dj} and $\Gamma_{+,j}$ partial yields of ion-stimulated desorption and partial fluxes for all kinds of positive ions existed in plasma. Combining Eqs. (1) and (2), the equation for etch rate may be obtained:

$$ER = \frac{\sum Y_{d,j}\Gamma_{+,j}(\gamma_{ch}S_F\Gamma_F + Y_s\Gamma_{Ar^+})}{\gamma_{ch}S_F\Gamma_F + \sum Y_{d,j}\Gamma_{+,j}} \quad (3)$$

To calculate the fluxes of neutral and charged particles to the surface, we used the methods described in Refs. 9. The probability of chemical reaction γ_{ch} may be approximated by the upper limit followed from the stoichiometry of reaction products (for example, $\gamma_{ch} = 0.5$ for Me-F₂) [10]. Similar to Refs. 11, we assume that Y_s and Y_d are a function of square root of ion energy, based on the collision cascade approximation for sputtering process:

$$Y_s = A(E^{1/2} - E_{0,s}^{1/2}), Y_d = B(E^{1/2} - E_{0,d}^{1/2}) \quad (4)$$

where A and B are parameters, which depend on type of ion and sputtered material, E is the incident ion energy, which is the sum of ion acceleration energy in plasma sheath and the negative DC bias voltage, applied to the substrate while $E_{0,s}$ and $E_{0,d}$ are threshold energies for sputtering and ion-stimulated desorption, respectively. The parameters A and $E_{0,s}$ for BST thin films sputtered by Ar⁺ ions may be extracted from Ref. 12 ($A = 0.13$, $E_{0,s} = 30$ eV). Parameters S_F, B and $E_{0,d}$ are not known exactly for BST, but the reasonable ranges for their deviation may be evaluated using an indirect literature data for well-studied systems, for example for F-SiO₂ and F-Si [11]. These ranges are 0.3-0.5, 0.1 and 4-10 eV for S_F, B and $E_{0,d}$, respectively.

Figure 3 shows the behaviors of both chemical and physical channels as a function of CF₄/Ar mixing ratio. As the Ar mixing ratio increases, the rate of physical sputtering increases monotonically and follows the behavior of Ar⁺ volume density.

It is important to note once more that the model we used cannot provide an exact quantitative agreement between measured and calculated etch rates in absolute scale due to simplifications in primary assumptions. Nevertheless, we can obtain a quantitative agreement in relative scale. Figure 4 shows the comparison for experimental and modeling data with a normalization point corresponding to pure Ar plasma. Calculations show that, in best case the model gives an outstanding description for relative behavior of BST etch rate in Ar-rich plasma, but systematically underestimates the etch rate in CF₄-rich plasma. One of the reasons may be connected with a chemical activity of CF_x radicals, which were not taken into account as reactants.

IV. CONCLUSION

In present work, we carried out an investigation of etching mechanisms for BST thin films in inductively coupled CF₄/Ar plasma. We have found that an increase of the Ar content in CF₄/Ar plasma leads to an increase in BST etch rate, which reaches a maximum value of 40 nm/min at 80% Ar. Langmuir probe measurements indicated weak influence of CF₄/Ar mixing ratio on both electron temperature and electron density. The analysis of surface kinetics demonstrated the possibility of non-monotonic etch rate behavior in the system with monotonic changes of fluxes of both chemically and energetically active species. It was found that the reason for etch rate maximum is the concurrence of physical and chemical pathways in ion-assisted chemical reaction.

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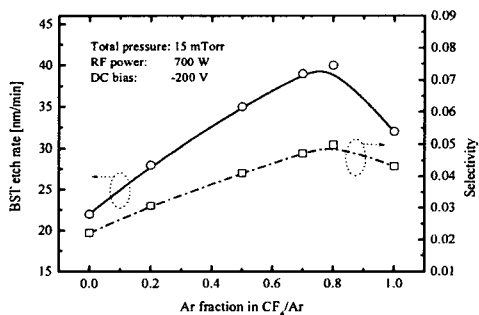


Fig. 1. BST etch rate and etch selectivity over PR as a function of CF₄/Ar mixing ratio.

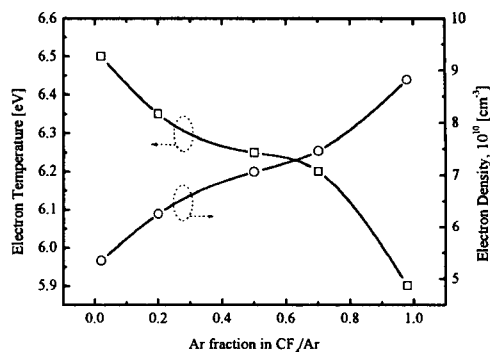


Fig. 2. Electron temperature and electron density determined by Langmuir probe measurements as a function of CF₄/Ar mixing ratio.

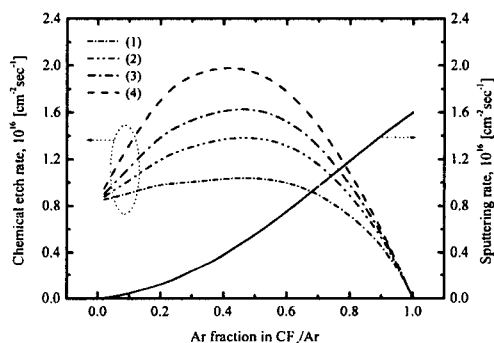


Fig. 3. Influence of CF₄/Ar mixing ratio on partial rates of ion assisted chemical reaction and physical sputtering as predicted by the model of surface kinetics.

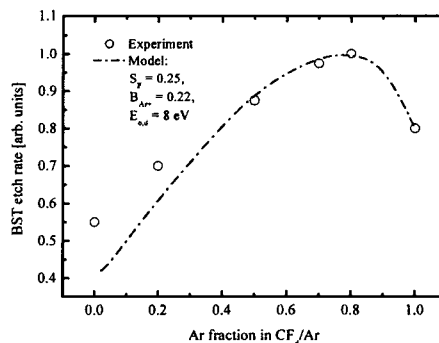


Fig. 4. Comparison of relative behavior of BST etch rate obtained by experiment and modeling.