ETCHING OF $Bi_{4-X}La_XTi_3O_{12}$ THIN FILMS IN CL_2/AR INDUCTIVELY COUPLED PLASMA

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Abstract

The etching properties of BLT inductively coupled plasma (ICP) was studied in terms of etch rate and selectivity as functions of Cl_2/Ar gas mixing ratio, rf power, dc bias voltage. We obtained the maximum etch rate of 803 Å/min at 20% Cl_2 addition into Ar plasma. The maximum etch rate may be explained by the simultaneously concurrence of physical sputtering and chemical reaction. The ion bombardment plays roles of destruction of metal (Bi, La, Ti)-O bonds to supply chemical interaction of metals with chlorine atoms, resulting in being desorbed only by ion bombardment. The variation of ion current density and of volume density for Cl and Ar atoms are measured by the optical emission spectroscopy (OES).

1. INTRODUCTION

Plasma etching systems have been widely used in microelectronics technology due to anistotropic etching characteristics. Reactive ion etching (RIE) reactors have been traditionally used systems for dry etching purposes because RIE systems shows high etching rates of materials formed low volatile etching products and appropriate selectivity. Nevertheless, RIE system has been limited their applications in ultra large-scale intergradations (ULSI) era owing to their sufficient disadvantages. First, it is evidently strong non-uniform radial distribution of volume densities of both charged and neutral particles. This fact causes low uniformity of etching process, which is especially critical for large-diameter wafers. Second, it is high electron temperature and impossibility of independent control of ion flux and ion bombardment energy. These parameters are closely connected with input power density and gas pressure. Therefore, RIE operations in low pressure region leads to sufficient ion bombardment energy (about 200 eV), resulted in producing radiational damages to the treated surface. However, inductively coupled plasma (ICP) system is practically free from disadvantages as mentioned above. Relatively low electron temperature in ICP reactor allows avoiding sufficient surface charging while ion flux and bombardment energy may be independently adjusted by input power a DC bias on lower electrode, which is used as substrate holder. In recent years, the majority of the plasma etching for ferroelectric thin films has been carried out using an inductively coupled plasma (ICP) etching system because of their advantages.

In recent years, high permittivity dielectrics for ferroelectrics random access memories (FRAM) have been studied intensively for wide rage of their applications such as IC-memory cards for digital camera due to low operating voltage and fast switching speed and non-volatility [1]. The chip architecture of FRAMs is very similar to DRAMS and ferroelectric thin films are employed instead of high-k films. Many researchers have studied candidate ferroelectric materials for application non-volatile random access memories. Bi-layered oxide perovskites, such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) have been intensively studied for use in FRAMs, because they show low leakage current, low coercive field and lack of fatigue with simple Pt electrodes and repeated polarization reversals with electric field cycling. In addition, BLT thin films exhibit low crystallization temperature, lack of fatigue and a medium polarization.

For the integration of ferroelectric thin films into high-density memories, numerous technology problems have to be solved. One main problem is that the stoichiometry control of both sidewalls and top area becomes very difficult at decreasing temperatures during deposition and etch process. Plasma etching of the ferroelectric thin films produces the nonvolatile etching by-products and the non-stoichiometric etching process must be avoided [2]. There are some reports in literature for etching PZT and SBT thin films using ICP etching system [3-4]. However, there is no report about etching mechanism and characteristics of BLT thin films as a function of gas chemistry.

In this paper, BLT thin films were etched with Cl_2/Ar gas in inductively coupled plasma (ICP) system. Etching characteristics on BLT thin films have been investigated in terms of etch rate and etch selectivity. The diagnostics of the Cl_2/Ar plasma were estimated using optical emission spectroscopy (OES) and Langmuir probe measurements.

2. EXPERIMENTAL DETAILS

The BLT thin films were prepared onto the Pt/Ti/SiO_2/Si substrate by MOD method. BLT thin films synthesized according to formula $Bi_{1-x}La_xT_3O_{12}$ (x=0.75). The precursors materials used to prepare the MOD method were bismuth acetate [$Bi(CH_3CO_2)_3$], lanthanum-acetate hydrate [$(CH_3CO_2)La{\cdot}xH_2O$], and titanium iso-propoxide {$Ti[OCH(CH_3)_2]_4$} and solvents were an acetic acid [CH_3CO_2H] and 2-methoxyethol [$CH_3OCH_2CH_2OH$], respectively. The molar composition was Bi : La : Ti = 3.25 : 0.75 : 3. A 10% excess amount of bismuth acetate was used to compensate the Bi-loss that occurred during annealing. The BLT film were deposited onto the Pt(120nm)/Ti(30nm)/SiO_2/Si substrate by a spinner operated at 4000 rev./min for 30 s and then dried at 400 ^oC for 10 min to remove organic material on a hot plate. The pre-baked film was annealed at various temperatures 550~750 °C for 1 h under an oxygen atmosphere for crystallization. The final thickness of BLT film was 200 nm.

The BLT thin films were etched as a function Cl_2/Ar plasma gas mixing ratio. The total flow rate was 20 sccm, rf power/dc-bias were 700W/150V and chamber pressure was 15 mTorr. Then, BLT thin films were etched as function of rf power and dc bias voltage at the fixed gas mixing ratio, at which we obtained the maximum etch rate. Etch rates were measured by using a α-step surface profiler [Tencor α-step 500]. The emission intensity of F and Ar atoms were investigated with using OES [NANOTEK NTS-U101] in order to understand the effects on the etch rate of BLT thin films as a function of gas mixing ratio in Cl_2/Ar plasma. The etching profile was investigated by scanning electron microscopy (SEM) [PHILIPS XL30SFEG].

3. RESULTS AND DISCUSSION

For the characterization of BLT thin films in an ICP system, the etch rate of BST and Pt as well as the selectivity BLT over PR and SiO_2 were systematically investigated as functions of gas mixing ratio, rf power and dc-bias voltage.

Figure 1 shows the etch rate of BLT and Pt as well as the selectivity of BLT to mask materials (SiO_2 and PR) as a function of Cl_2/(Cl_2+Ar) mixing ratio. As the Cl_2 gas mixing ratio increases up to 20 %, the etch rate of BLT and Pt increased. However, with furthermore increasing Cl_2 content over 20 %, the etch rate of BLT and Pt decreased. As a result, dependence of etching rate on Cl_2/Ar mixing ratio is characterized by extreme behavior with a maximum of 803 /min corresponding to Cl_2/(Cl_2+Ar) of 0.2.

Figure 2 shows the etch rate of BLT and Pt as well as the selectivity of BLT to mask materials (SiO_2 and PR) as a function of dc-bias voltage. As the dc-bias voltage increases from 50 V to 200 V, the etch rate of BLT and Pt increases from 270 /min to 910 /min and 450 /min to 930 /min, respectively.

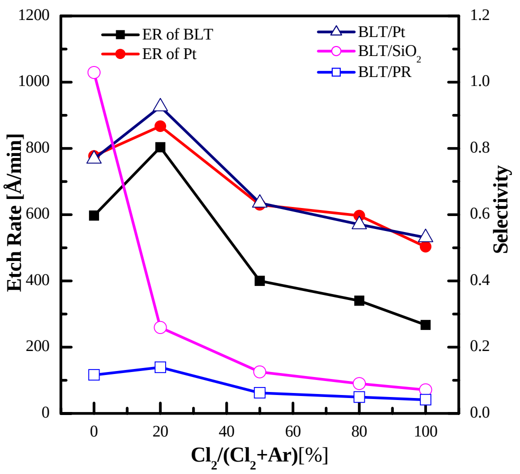

Fig. 1. The etch rate of BLT and Pt as well as the selectivity of BLT to Pt and SiO_2 as a function of Cl_2/(Cl_2+Ar) mixing ratio.

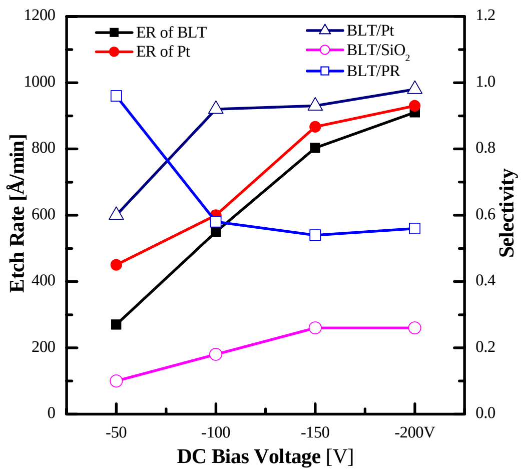

Fig. 2. The etch rate of BLT and Pt as well as the selectivity of BLT to Pt and SiO_2 as a function of dc bias voltage.

Analysis of etching rate data allows to formulate some assumptions concerning etching mechanism. Generally speaking, in Cl_2/Ar plasma, etching process is supported by two mechanisms such as physical sputtering and chemical reaction between Cl atoms and metal components of BLT film. It is important to note that according to our data maximum etching rate is obtained in pure Ar plasma. Therefore it seems that physical sputtering by argon ion bombardment makes dominant contribution in etching process. Low contribution of chemical reaction is rather expectable and connected with very low volatility of La chlorides. This compounds have a low pressure of saturated vapors so that spontaneous thermal desorption is expected as negligible. Nevertheless, under the conditions when ion bombardment is able to supply cleaning of the treated surface from reaction products, contribution of chemical etching may be more than expected. In frameworks of these assumptions, presence of maximum on etching rate dependence on Cl_2/Ar mixing ratio may be caused by at least two reasons: acceleration of ion bombardment of increasing of efficiency of chemical reaction.

To investigate the influence of mixture content on relative densities of active species we used OES analysis. Figure 3 shows the emission intensities of the several species as a function of the Cl_2 fraction in the Cl_2/Ar plasma. In general case, emission intensity reflects not only volume density of corresponding particles but depends on excitation coefficient and electron density too. Nevertheless, as it shown in Fig.3, intensity of Ar line changes directly proportional to Ar content in plasma mixture. It means that in our case increasing of Ar mixing ratio either not influence on excitation constant and electron density or these parameters have opposite tendencies and compensate each other. Therefore it is possible to assume that emission intensities plotted in Fig.3 reflects the behavior of volume densities of corresponding particles. Therefore presence of maximum on emission intensity of Cl atoms may be preliminary related to same behavior of volume density of Cl atoms although correct conclusion requires additional investigations. In this framework, extreme etching rate behavior is related to acceleration of chemical etching mechanism. Decreasing of etching rate with Cl_2 addition more than 20% may be explained by decreasing of ion flux on the treated surface that affects on sputtering efficiency as well as on ion enhanced desorption of reaction products. Note, that XPS analysis of etched films showed accumulation on the surface of metal-chlorides with increasing of Cl_2 content in Cl_2/Ar mixture.

Figure 4 shows cross-sectional SEM images of BLT thin films etched in Cl_2 (20)/Ar(80) plasmas. To fabricate high-density FRAM devices, etch processes require stringent critical dimension control and steep etch profiles over 70°. As shown in Fig 4, the etch profile in Cl_2(20)/Ar(80) plasma is over 75°and there are no ears on the corner of BLT thin films.

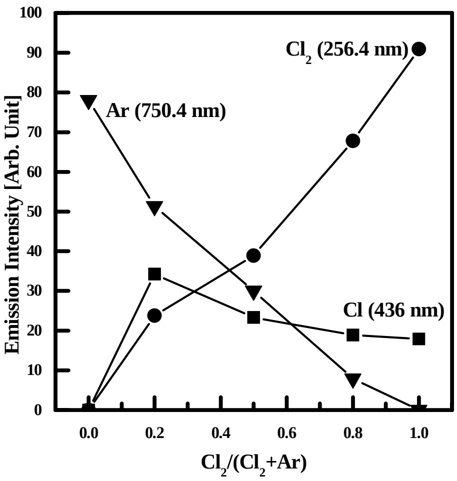

Fig. 3. The etch rate of BLT and Pt as well as the selectivity of BLT to Pt and SiO_2 as a function of $Cl_2/(Cl_2+Ar)$ mixing ratio.

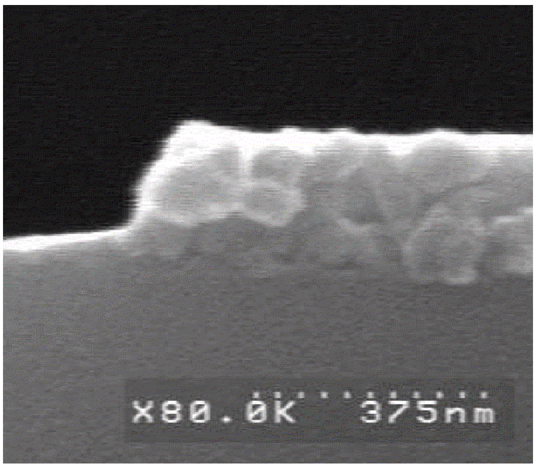

Fig. 4. The cross-sectional SEM images of BLT thin films etched in $Cl_2/(Cl_2+Ar) = 0.2$

4. CONCLUSION

The effect of Cl_2/Ar plasma on BLT thin film etching was studied. We obtained a maximum etch rate of 803 Å/min at Cl_2/Ar of 0.2. The presence of maximum on etching rate dependence on Cl_2/Ar gas mixing ratio may be explained by variation of volume density for Cl atoms and by the concurrence of two etching mechanisms such as physical sputtering and chemical reaction with formation of low-volatile products, which can be desorbed only by ion bombardment. In addition, the roles of ion bombardment include destruction of metal (Bi. La, Ti)-O bonds to supply chemical interaction of metals with chlorine atoms. These conclusions are consistent with the results of OES analysis.

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