BCl_3/N_2 유도결합 플라즈마로 식각된 PZT 박막의 식각 특성

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Dry etching properties of PZT thin films in BCl_3/N_2 plasma

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Abstract

The dry etch behavior of PZT thin films was investigated in BCl_3/N_2 plasma. The experiments were carried out with measuring etch rates and selectivities of PZT to SiO_2 as a function of gas concentration and input rf power, chamber pressure. The maximum etch rate was 126 nm/min when 30% N_2 was added to BCl_3 chemistry. Also, as input rf power increases, the etch rate of PZT thin films was increased. Langmuir probe measurement showed the noticeable influence of BCl_3/N_2 mixing ratio on electron temperature and electron density as input rf power increased. The variation of Cl radical density as plasma parameters changed was examined by Optical Emission Spectroscopy (OES) analysis. According to X-ray diffraction (XRD) analysis, PZT thin films were damaged in plasma and an increase in (100), (200) and (111) phases showed the improvement in structure of the PZT thin films after the O_2 annealing process.

Key Words : Etching, PZT, Ferroelectric properties.

I. INTRODUCTION

For many years, the lead zirconate titanate ($Pb(Zr,Ti)O_3$) thin films have been extensively studied as capacitor materials in nonvolatile ferroelecric random access memory (FRAM). [1] In order to realize highly integrated FRAMs involving PZT thin films, the etching process of PZT thin films with high etch rate, vertical etch profile, and low by-product must be developed. Many researchers have studied the etching of PZT films using reactive ion etching (RIE), magnetically enhanced reactive ion etching (MERIE), helicon plasma, electron cyclotron resonance (ECR) and inductively coupled plasma (ICP). Especially, ICP provide a high degree of anisotropy, high etch rate, stoichiometry control, and good selectivity with great process control and the ICP provides lower ion energy and the capability of operating at lower chamber pressure.] However, high-density plasma etching have the negative features such as changes of the chemical structure by etching, chemical residue contamination and damage of the crystal structure due to bombardment by high-energy ions.

In this paper, the PZT thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by sol-gel process. We observed the effect of etching properties in the PZT thin films during etching in BCl_3/N_2 plasma. Also, the etch rate was measured by varying the etching parameters such as gas mixing ratio, rf power. Etching characteristics on the PZT thin films have been investigated in terms of etch rates and etch selectivity over SiO_2. Plasma diagnostics was performed by both Langmuir probe (LP) and optical emission spectroscopy (OES). The structural damages to the near surface of PZT are evaluated by x-ray diffraction (XRD).

II. EXPERIMENTAL

The PZT thin films were prepared on

Pt/Ti/SiO_2/Si (100) substrates by using sol-gel processes. The PZT (30/70) precursor solution was spin-coated on a substrate by a spinner operated at 3500 rpm for 30 s. After coating, pyrolysis is followed on the hot plate maintained at 350 °C for 10 min to remove organic materials. The spin coating and drying was repeated to obtain the desired thickness for the PZT thin films of 250 nm. Amorphous films were sintered at 650 °C for 1 h to crystallize them into a perovskite structure in a preheated furnace. The PZT thin films were etched with BCl_3/N_2 gas chemistry. The gas-mixing ratio was varied to investigate the characteristics of etching. For these experiments, the total gas flow, chamber pressure, top rf power, bottom dc-bias voltage, and substrate temperature was 20 sccm, 1.3 Pa, 700 W, -200 V and 20 °C, respectively. In addition, plasma etching of the PZT thin films was investigated by changing the etching parameter including top rf power 500 ~ 800 W with the fixed BCl_3/N_2 gas-mixing ratio. The etch rate was measured by the surface profiler (KLA Tencor, a-step 500). Plasma diagnostics was performed by Langmuir probe (LP) and optical emission spectroscopy (OES). LP measurements were carried out using single, cylindrical, and rf-compensated probe (ESPION, Hiden Analytical). For the treatment of 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. In order to investigate the effect of etching damage on PZT thin films, the crystal structure was observed with XRD (Rigaku).

III. RESULT AND DISCUSSION

The PZT thin films were etched with various BCl_3/N_2 gas chemistry at a substrate temperature of 20 °C, ICP rf power of 700 W, dc-bias voltage of -200 V and chamber pressure of 1.3 Pa. The gas mixture used was chosen for the following reasons. The main active component, Cl, provides a high degree of dissociation and leads to the formation of metal chlorides, which are generally more volatile than metal fluorides. And, Cl_2/N_2 chemistry in an ICP process resulted in decreased etch rates. This is due to less available reactive Cl. [8] However, addition N_2 to BCl_3 chemistry resulted in increased etch rates up. It is suggested that N_2 enhanced the dissociation and the ionization of BCl_3. This resulted in higher concentrations of reactive Cl and Cl ions and faster etch rates both from the chemical and physical bombardment combinations. [9] Fig. 1 shows the behavior of the etch rates of PZT, SiO_2 as a functions BCl_3/N_2 mixing ratio. As the content of N_2 in gas mixture increases, the etch rate of the PZT thin films increases and reaches a maximum when 30% N_2 was added to BCl_3 chemistry. Its value was 126 nm/min and the selectivity of the PZT thin films to SiO_2 was 1.2. Further addition of N_2 into BCl_3 leads to rapid decrease of PZT etch rate. As the result, we obtained almost fourfold difference between the etch rates in pure BCl_3 plasma and pure N_2 plasma. It shows that the chemical reaction between Cl radicals and the surface of PZT films plays important role in the PZT etching process. Also, the addition of N_2 increases the generation of Cl radicals in plasma and the ion bombardment that effectively removes nonvolatile

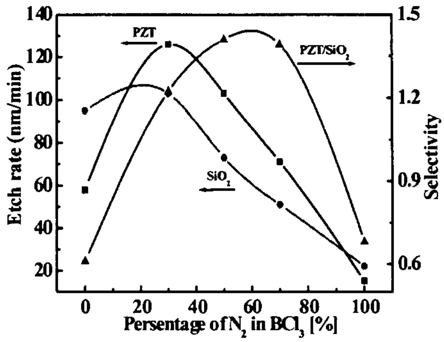

Figure 1. Etch rate and selectivity of PZT thin films in BCl_3/N_2 plasma.

etching by-products such as metal chlorides. Therefore, we suppose that ion-assisted chemical etching is effective for etching PZT thin films.

Figure 2 illustrates the influence of BCl_3/N_2 mixing ratio on electron temperature and electron density extracted from LP measurements. As N_2 content in BCl_3/N_2 mixture increases, electron temperature decreases while electron density increases. Electron temperature influences to the number of electron impact process, and electron impact processes are characterized by threshold energies both concerning ionization and excitation. Because of the high values of ionization potentials for N2 (15.58 eV), the increase of N_2 content in BCl_3/N_2

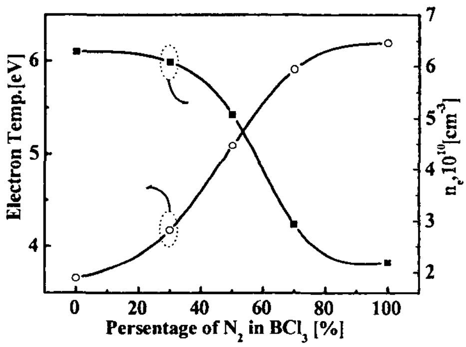

Figure 2. Electron temperature and electron density as a function of BCl_3/N_2 gas mixing ratio.

mixture increases the number of electron impact processes with higher thresholds and results in domination of more "fast" electrons in electron energy distribution function (EEDF). Therefore it is supposed that more available Cl radicals are produced. For the electron density, the behavior of this parameter may be explained by the decrease of total ionization rate and by the increase of electron diffusion coefficient due to the growth of electron temperature.

Figure 3 shows the etch rate of PZT, SiO_2 and the selectivity of PZT to SiO_2 as a function of varying ICP rf power under 70 % BCl_3 in BCl_3/N_2 plasma. Other parameters were same to

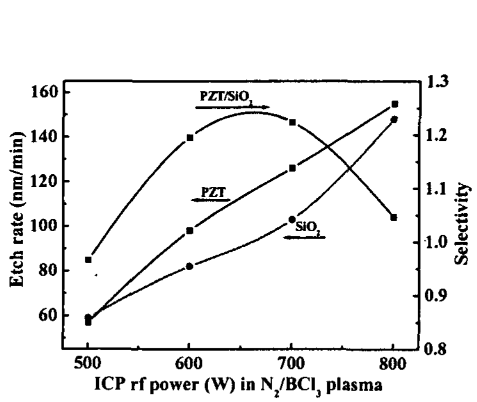

Figure 3. Etch rate and selectivity of PZT thin films as a function of applied rf power.

Fig.1 As ICP rf power was raised from 500 to 800 W, the etch rate of PZT increased from 57 to 155 nm/min. This result may be attributed to the influence of input power to BCl_3 dissociation degree, ionization rate and volume density of positive ions. That is, an increase of input rf power leads to an increase of reactive radical and ion, which increases PZT etch rate.

Figure 4 shows that the variation of emission intensities for Cl measured using OES when rf power and chamber pressure change. We measured the emission intensities of Cl (452.6 nm, $4p^1{}_{3/2} \rightarrow 4s_{3/2}$, 10.7 eV). It is well known that the main excitation mechanism for all lines is a direct electron impact processes. The excited state emission from Cl increases with an increase in N_2 and exhibit maxima at 30% N_2. As rf power increases, the Cl radical density is increased. Considering that the dominant species in PZT etch process is reactive Cl, this data is reasonable. That is, higher concentration of active species in the plasma leads to higher etch rate.

In order to investigate the etching damage to PZT thin films, we observed the crystal structure of various etching conditions with using XRD patterns as shown in Fig. 5. It can be seen that XRD pattern for as-deposited PZT thin ■lms shows a polycrystalline structure. After the etching in BCl_3(70%)/N_2(30%) plasma, the intensities for all the peaks were sufficiently

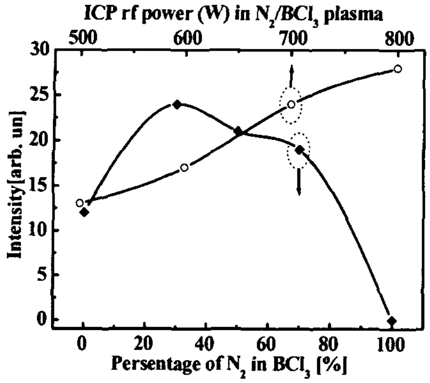

Figure 4. Optical emission intensities measured by OES as a function of rf power and chamber pressure.

lower. Especially, the peak in BCl_3(70%)/Ar(30%) plasma is low as compared with the peak in BCl_3/N_2 plasma. We assume that this result is the reason why BCl_3/Ar plasma produces more significant damage of the crystalline structure due to the intensive ion bombardment by the Ar ions is heavier than N_2 ions.

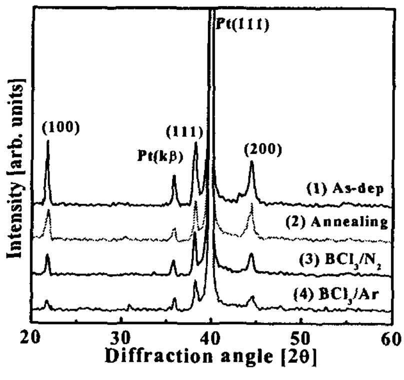

Figure 5. The XRD pattern of as-deposited, etched and re-annealed PZT thin films. (1) as-deposited PZT thin film (2) annealing at 650 ℃ for 10 min (3) PZT thin film etched in BCl_3/N_2 plasma. (4) PZT thin film etched in BCl_3/Ar plasma.

IV. CONCLUSION

In this study, Etching characteristics of the PZT thin films were investigated in terms of etch rate, selectivity using BCl_3/N_2 plasma. Using Langmuir probe measurements, addition of N_2 occurs the increase of electron temperature while electron density decreases. These effects are explained by the influence of BCl_3/N_2 mixing ratio on electro-physical properties of plasma. And it was investigated that the addition of N_2 and the increase of rf power leads to increase of Cl radicals by using OES analysis. These results show that ion-assisted etching mechanism confirms the possibility of non-monotonous etch rate behavior due to the concurrence of physical chemical channels in etching process. XRD analysis indicated that the damage of PZT thin films was induced by plasma and the improvement in the structure after annealing is accompanied.

REFERENCE

[1] G.H. Haerting, J. Vac. Sci. Technol. 9 (1998) 414.

[2] R.J. Shul and C.G. Willinson, M.M. Bridges, J. Han, J.W. Lee, S.J. Pearton, C.R. Abernathy, J.D. McKenzie, S.M. Donovan, L. Zhang, and L.F. Lester, J. Vac. Sci. Technol. A 16 (1998) 1621.

[3] F. Ren, J.R. Lothian, J.M. Kuo, W.S. Hobson, J. Lopata, J.A. Caballero, S.J. Pearton, and M.W. Cole, J. Vac. Sci. Technol. B14 (1995) 1.