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Etching characteristics of lead magnesium niobate–lead titanate (PMN–PT) relaxor ferroelectrics

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Abstract

Etching characteristics of Pb$\{(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}\}O_3$ (PMN–PT) were studied by an inductively coupled plasma etcher using Ar, Cl_2, and BCl_3 gas combinations. Using Ar/BCl_3 and Cl_2/BCl_3, PMN–PT etch rates higher than 2500 Å/min could be obtained with the etch selectivity over photoresist higher than 1.0. In general, the increase of BCl_3 in Ar/BCl_3 and Cl_2/BCl_3 increased etch selectivity without decreasing PMN–PT etch rates significantly. X-Ray photoelectron spectroscopic analysis revealed that, during the PMN–PT etching, Ar ion bombardment enhanced the etching of Pb and Ti components preferentially, BCl_3 plasma enhanced the etching of O, Nb, and Mg components, and Cl_2 plasma enhanced the etching of Pb component. The etched profile angle of PMN–PT increased with the increase of PR selectivity. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PMN–PT; Inductively coupled plasma; Plasma etching; Oescoptical emission spectrometry; Cl radical

1. Introduction

Ferroelectric thin films have various properties such as high permittivity, piezoelectricity, electro-optic property, pyroelectricity, polarizability, etc., and, due to these extensive properties, these films recently have been intensively investigated for various applications [1,2]. Among these properties, the piezoelectric property of ferroelectric thin films makes them ideal for micro actuators. In the fabrication of micro actuators, Pb$(Zr_xTi_{1-x})O_3$ (PZT) films are generally used, however, due to the potential problem of PZT thin films in their fatigue and aging characteristics, many researchers are currently being carried out to develop new materials which can replace PZT thin films [3–5]. One of the well-known candidates is the Pb$\{(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}\}O_3$ (PMN–PT) thin film [6]. To adapt this material to the micro actuators, not only piezoelectric properties but also other processing properties such as etching characteristics need to be investigated. Due to the relatively new introduction of PMN–PT thin films to the micro actuators, almost no studies on the etching characteristics of Pb$\{(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}\}O_3$ (PMN–PT) can be found in the literature. Especially, dry etching characteristics of PMN–PT which may be required for the fabrication of next generation micro actuators have never been reported.

In this study, dry etching characteristics of PMN–PT ferroelectric thin films were investigated using inductively coupled plasmas and their etching mechanism was investigated using plasma diagnostic tools such as optical emission spectroscopy and Langmuir probe. The purpose of this study is to investigate a feasibility of using a dry etching technique in the fabrication of PMN–PT based micro actuators.

2. Experiment

PMN–PT ferroelectric thin films with a perovskite phase were prepared on PT (lead titanate)/Pt/Ti/LTO/nitride/Si substrates using a sol–gel method. The PMN–PT thin films were mixture of $(PMN)_{0.9}$ and $(PT)_{0.1}$, because of good piezoelectric

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property at this composition. Samples were patterned using a positive photoresist with the thickness of 1.2 μm (AZ1512) or Cr and etched by an inductively coupled plasma etcher described elsewhere in detail [7]. Main etch gas mixtures used in this experiment were the combination of Cl_2, Ar, and BCl_3. To focus on the etching characteristics as a function of gas ratio, other etching parameters such as coil RF power, substrate bias, operational pressure, and substrate temperature were maintained at 600 W, −200 V, 20 mtorr, and 70°C, respectively. The etch rates were determined from the etch depth measurement using a surface profilometer. To investigate the surface stoichiometry of the etched PMN–PT thin films, X-ray photoelectron spectroscopy (Fisons Instruments Surface Systems; ESCALAB 220i) was used and the PMN–PT etched profiles were observed by scanning electron microscopy (HITACHI; S-2150). To diagnose the plasmas that were used to etch PMN–PT thin films, optical emission spectroscopy (SC Technology; PCM 402) and a Langmuir probe (Electro Static Probe; Hiden analytic Inc.) were used.

3. Results and discussion

The purpose of this experiment is to study the dry etching properties of PMN–PT and to investigate the possible etching mechanism. To understand the general etching properties, the etch gas combinations were varied while maintaining other etch parameters such as RF power, substrate bias voltage, operational pressure, and substrate temperature at 600 W, −200 V, 20 mtorr, and 70°C, respectively. When PMN–PT thin films were etched using pure gases such as Ar, HBr, Cl_2, CHF_3, BCl_3, H_2, and CF_4, the PMN–PT etch rates less than 800 Å/min were obtained for HBr, CHF_3, H_2, and CF_4. However, in the case of Ar, Cl_2, and BCl_3, the PMN–PT etch rates were higher than 1200 Å/min and the etch rate with BCl_3 was higher than 2400 Å/min. Therefore, the gas combinations composed of Ar, Cl_2, and BCl_3 were investigated to study the effects of gas mixture on the etch properties.

Fig. 1a shows the etch rates of PMN–PT and the etch selectivities over photoresist as a function of Cl_2/Ar gas mixture. The addition of Ar to Cl_2 up to 20% increased the etch rate rapidly, however, the further increase of Cl_2 did not affect the etch rate significantly. In Fig. 1b, reactive radicals and ion densities in the Cl_2/Ar plasmas were investigated for the etching conditions in Fig. 1a using optical emission spectroscopy and a Langmuir probe, respectively. In the case of reactive species, an optical emission peak of chlorine radical observed at 754.7 nm was investigated and, in the case of ion densities which can affect the physical ion bombardment to the surface of PMN–PT, ion saturation current densities directly measured from the Langmuir probe biased at −40 V were used as a measure of ion densities. As shown in Fig. 1b, the increase of Cl radicals with the increase of Cl_2 percentage showed the similar trend as the etch rate while the ion current density decreased exponentially. The decrease of ion current density with the increase of chlorine appears to be related to the decrease of Ar^+ significantly compared to the increase of Cl_2^+ and Cl^+ with the increase of Cl_2 percent. In the etching of PMN–PT, the ion bombardment is required to break the bonding in the specimen, however, from the figure, it appears that, in our experimental conditions, the density of chlorine radicals appears to control the PMN–PT etch rate. The etch selectivity over photoresist was generally lower than 0.6.

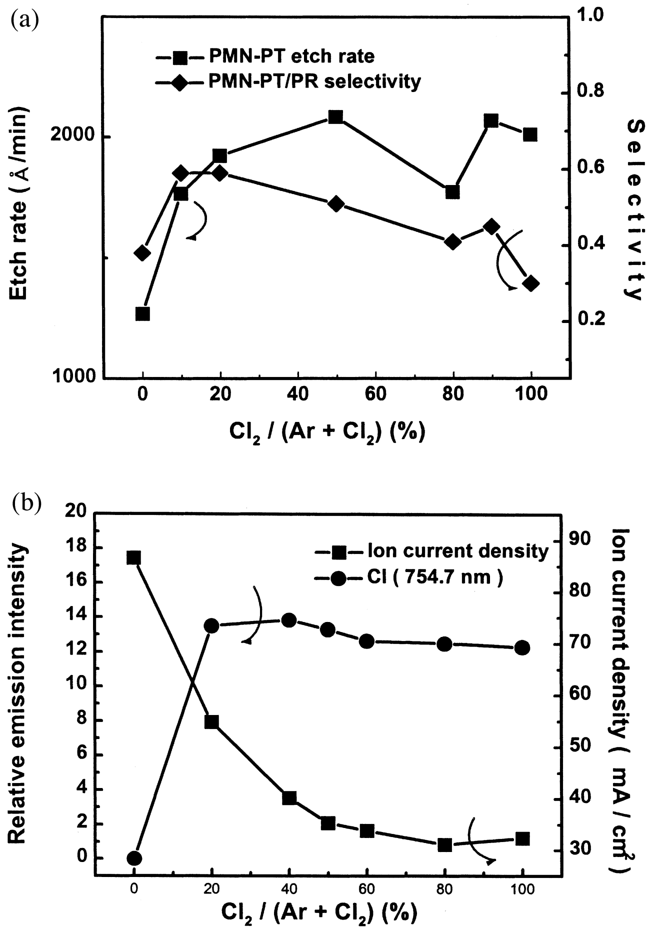

Fig. 1. (a) Etch rates of PMN–PT and etch selectivities over photoresist as a function of Ar/Cl_2 gas mixture. RF power: 600 W; DC-bias voltage: −200 V; operational pressure: 20 mtorr; substrate temperature: 70°C. (b) Relative optical emission intensities of Cl (754.7 nm) and ion current densities as a function of Ar/Cl_2 gas mixture.

To improve the etch selectivity over photoresist, other gas combinations such as BCl_3/Ar and BCl_3/Cl_2 were used. Fig. 2a shows PMN–PT etch rates and selectivities over photoresist with the gas combination of BCl_3/Ar. As shown in the figure, with the increase of

BCl_3 to 20% in the BCl_3/Ar gas mixture, the etch rate increased more than two times and the further increase of BCl_3 slowly decreased the etch rates. However, the etch selectivity generally increased with the increase of BCl_3 percentage up to approximately 1.6. Using OES and the Langmuir probe, the characteristics of BCl_3/Ar plasmas were also investigated and the results are shown in Fig. 2b. In the case of OES, the radical peak of BCl observed at 271.8 nm were included in addition to the Cl radical peak. In fact, there are more reactive radicals dissociated from BCl_3 such as B, Cl, and BCl_2 in addition to BCl, and these could be observed using a quadrupole mass spectrometer (QMS) [7]. However, their trends with the addition of BCl_3 were similar among radicals except for the Cl radical and BCl_2 appeared to be the most abundant species among BCl_3 radicals. Also, the data trends obtained from both OES and QMS were similar to each other. Therefore, only the peak related to BCl was shown in the figure in addition to the peak related to Cl. As shown in the figure, the peak intensity of Cl radicals was the highest near 20% of BCl_3. The peak intensity of BCl increased until approximately 40% of BCl_3 and the further increase of BCl_3 saturated the peak intensity of BCl radical. In the case of ion current density measured by the Langmuir probe, it decreased exponentially similar to the case with Cl_2/Ar. From the figure, the decrease of ion densities and the increase of BCl_x appear to assist in increasing the etch selectivity by decreasing the photoresist etch rate [8]. Especially, BCl_x radicals are known to recombine with oxygen and form B_xO_y or BCl_xO_y, therefore, appear to reduce oxygen which enhances photoresist etch rates, and increase the etch selectivity. Also, the formation of oxygen compound with BCl_x can increase the PMN–PT etch rates by removing oxygen from the surface of PMN–PT where oxygen consists of 60% of PMN–PT compositions. Therefore, not only chlorine radicals dissociated from BCl_3 but also BCl_x appear to participate in the etching of PMN–PT.

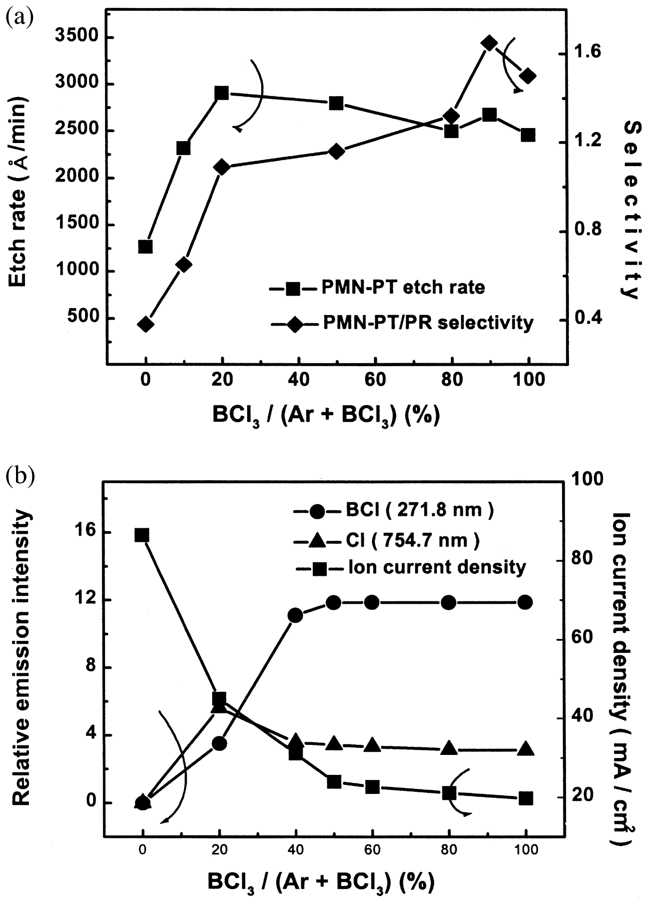

Fig. 2. (a) Etch rates of PMN–PT and etch selectivities over photoresist as a function of Ar/BCl_3 gas mixture. RF power: 600 W; DC-bias voltage: −200 V; operational pressure: 20 mtorr; substrate temperature: 70°C. (b) Relative optical emission intensities of Cl (754.7 nm) and BCl (271.8 nm), and ion current densities as a function of Ar/BCl_3 gas mixture.

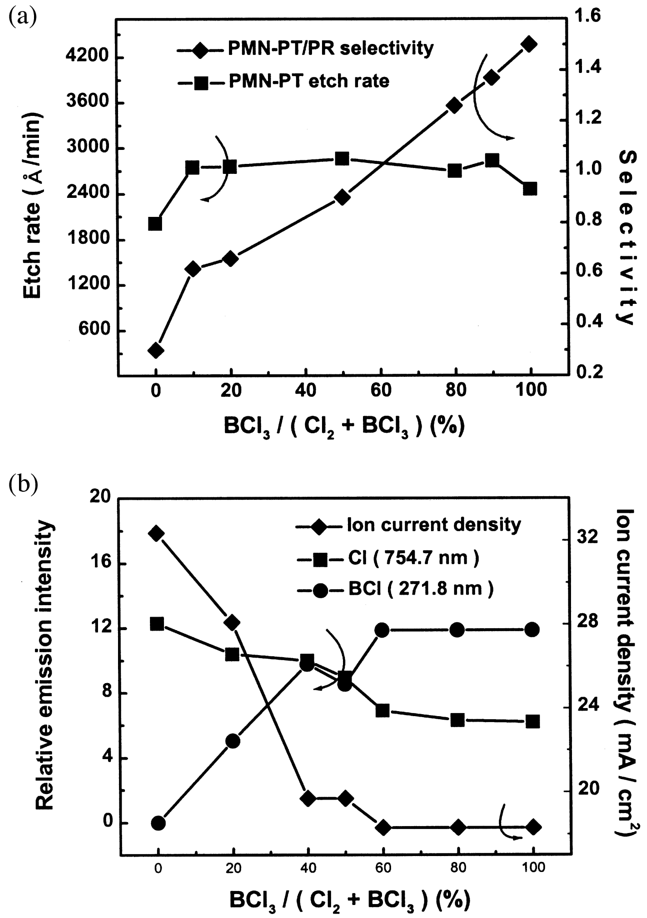

Fig. 3. (a) Etch rates of PMN–PT and etch selectivities over photoresist as a function of Cl_2/BCl_3 gas mixture. RF power: 600 W; DC-bias voltage: −200 V; operational pressure: 20 mtorr; substrate temperature: 70°C. (b) Relative optical emission intensities of Cl (754.7 nm) and BCl (271.8 nm), and ion current densities as a function of Cl_2/BCl_3 gas mixture.

The effect of BCl_x on the etching of PMN–PT can be more clearly seen from the etching with BCl_3/Cl_2

gas mixtures and the results are shown in Fig. 3a,b. As shown in the figure, even though Cl radicals are decreased with the increase of BCl_3 percentage, the PMN–PT etch rates appear to increase initially and maintain at that etch rates with the further increase of BCl_3. The decrease of etch rate caused by the decrease of Cl radicals appears to be compensated by the increase of etch rate by the increase of BCl_x radicals and more possibly by BCl_2 radicals. Also, the increase of BCl radicals with the decrease of ion current density appears to increase the etch selectivity almost linearly with the increase of BCl_3 percentage similar to the case of Fig. 2.

To understand etch mechanism better, the surface compositions of PMN–PT etched using various gas combinations were investigated using XPS and the results are shown in Table 1. As a reference, the surface composition of the non-etched PMN–PT sample was also included. As shown in the table, Pb and Ti were preferentially removed by Ar ion bombardment from the surface of PMN–PT, Pb was removed by Cl_2, and O, Nb, and Mg were removed by BCl_3. The use of the gas mixture showed the combined effect of preferential removal from each plasma species. The effect of BCl_3 plasma on the removal of oxygen from PMN–PT

Table 1
X-Ray photoelectron spectroscopic (XPS) results of PMN–PT surfaces etched using Ar, Cl_2, and BCl_3 gas mixtures

	Element % on the etched surface				
	O	Ti	Nb	Pb	Mg
Control	60	2	12	20	6
Ar100%	80.3	1.1	9.6	1.8	7.2
$Cl_2$100%	67.8	1.8	11.2	10.8	8.4
$BCl_3$100%	45.6	11.8	3.5	36.1	3.0
Ar50%/$Cl_2$50%	74.3	1.1	10.7	5.2	8.7
Ar50%/$BCl_3$50%	60.5	5.5	8.7	20.7	4.6
$Cl_2$50%/$BCl_3$50%	46.2	11.0	2.0	39.4	1.4

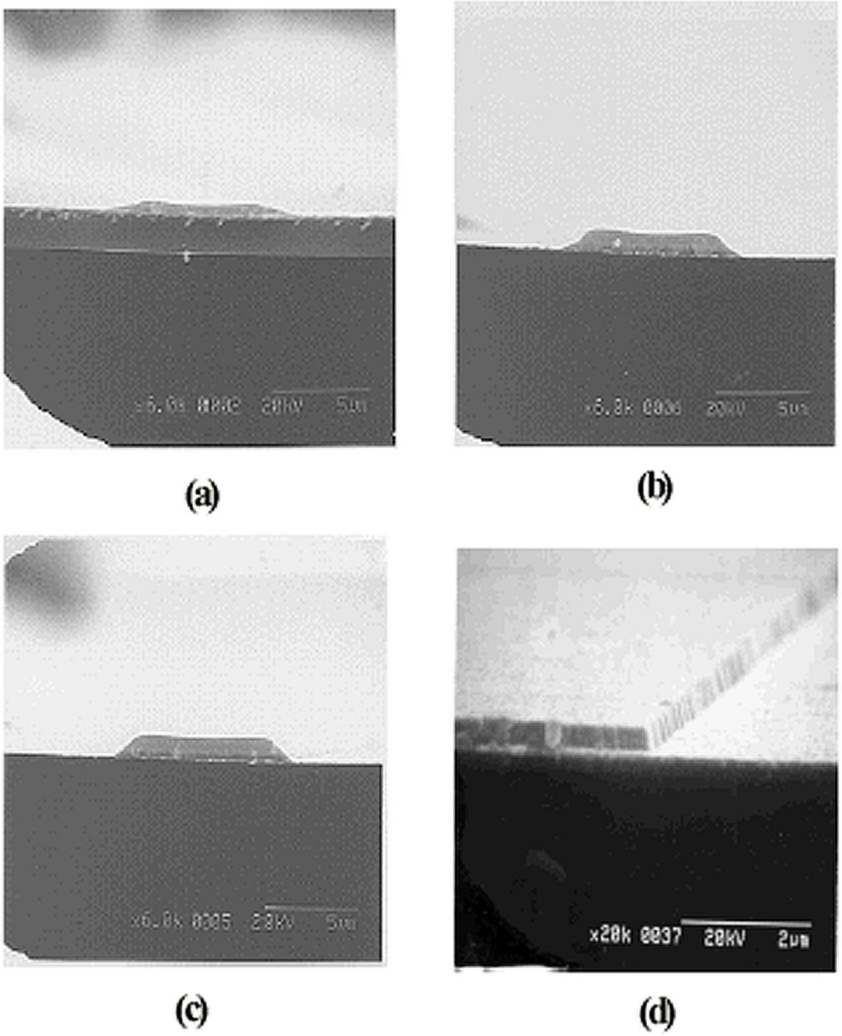

Fig. 4. SEM micrographs of the etched PMN–PT thin films. The etch profiles are shown for the etching with (a) Ar50%/$Cl_2$50%, (b) $Cl_2$50%/$BCl_3$50%, and (c) Ar50%/$BCl_3$50% with a photoresist mask and (d) Ar50%/$BCl_3$50% for Cr mask.

can be clearly seen from the table, and which appears to enhance the PMN–PT etch rate. The etched surface which is the closest to the stoichiometric composition could be obtained from the etching by Ar50%/$BCl_3$50%. It is believed that near stoichiometric composition could be obtained with reasonable etch rates and selectivities using suitable gas combinations of Ar/Cl_2/BCl_3.

Using different gas mixtures, PMN–PT thin films masked with 1.2 μm thick photoresist or Cr were etched and their etch profiles were observed using SEM. Fig. 4 shows the profiles of PMN–PT etched using (a) Ar50%/$Cl_2$50%; (b) $Cl_2$50%/$BCl_3$50%; (c) Ar50%/$BCl_3$50% for photoresist mask; and (d) Ar50%/$BCl_3$50% for Cr mask. Due to the increase of etch selectivity from (a) to (c) [selectivity: (a) 0.6, (b) 0.9, and (c) 1.2] for the same photoresist mask, the etch profile was improved and the use of Cr as an etch mask showed almost a vertical etch profile as shown in Fig. 4d.

4. Conclusions

In this study, PMN–PT thin films which can be applied to micro actuators were etched using various gas mixtures and their etch properties were investigated using OES and Langmuir probe for plasma characterization and using XPS for surface characterization. As the etching parameters, gas combinations of Ar, Cl_2, and BCl_3 were used while other etch parameters were maintained the same.

The etch results showed that, in our experimental conditions, the amount of Cl radicals dissociated from Cl_2 or BCl_3 appears to be important in the etching of PMN–PT rather than the amount of ion densities bombarding the surface. Also, in the etching with BCl_3, BCl_x which can recombine with oxygen in the plasma and on the PMN–PT surface increased the etch selectivity over photoresist in addition to the increase of PMN–PT etch rates. The selective removal of oxygen by BCl_3 plasma could be observed from the investigation of the etched surface of PMN–PT. Using BCl_3 rich, Ar/BCl_3 gas mixtures and BCl_3 rich, Cl_2/BCl_2 gas mixtures, PMN–PT etch rates higher than 2500 Å/min could be obtained with the etch selectivities over photoresist higher than 1.0.

Acknowledgements

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