

# A study of lead zirconate titanate etching characteristics using magnetized inductively coupled plasmas

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## Abstract

In this study,  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) thin films were etched using magnetized inductively coupled plasmas (MICP) and their etch characteristics were compared with those by non-magnetized conventional inductively coupled plasmas (ICP). The use of Helmholtz type axial electromagnets around the chamber wall increased the PZT etch rates while decreasing etch uniformity. By using both the multidipole magnets and the axial electromagnets around the chamber wall, the etch uniformity could be improved while maintaining high PZT etch rates. PZT etch rates close to  $1700 \text{ \AA}/\text{min}$  which are three times higher than those etched using the conventional ICP plasmas could be obtained with optimized MICP conditions. The etch selectivities over Pt at these conditions were higher than 1.5. The MICP used in the experiment showed higher Cl radicals and  $\text{Cl}_2^+/\text{Cl}^+$  ratios in the plasmas compared with those in the conventional ICP plasmas. Therefore, the increased chemical and/or physical sputtering by the increased  $\text{Cl}_2^+/\text{Cl}^+$  ratios along with the increased chemical reactivity by higher Cl radical densities appears to be responsible for high PZT film etch rates obtained with the MICP in our study. Using the MICP in  $90\% \text{Cl}_2 + 10\% \text{Ar}$  gas mixture, a nearly vertical etch profile could be also obtained. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Lead zirconate titanate; Magnetized inductively coupled plasmas; Etching

## 1. Introduction

Ferroelectric thin films, which have large piezoelectricity, are currently paid much attention due to their applications in microelectro-mechanical systems (MEMS) [1,2]. In the fabrication of these devices, the etching of ferroelectric thin films has been mostly conducted by chemical wet etching. Recently, several studies have been reported on the application of dry etching processes, including ion beam etching, plasma etching and reactive ion etching (RIE) to ferroelectric or paraelectric thin films such as  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) or  $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$  (BST) using halogen-containing gases [3–9]. However, low etch rates and poor etched profiles remain problems to be solved.

Therefore, in this study, PZT film etch characteris-

tics in a magnetized inductively coupled plasma (MICP), which was confined by magnetic fields formed using multidipole permanent magnets and Helmholtz type electromagnets around the chamber wall, were studied to improve PZT etch rates for the application of MEMS devices. The etch characteristics were compared with those obtained without the magnets, i.e. conventional inductively coupled plasmas (ICPs).

## 2. Experiment

A schematic view of the apparatus used in this study is shown in Fig. 1. Radio frequency power (13.56 MHz, 0–1200 W) was supplied to the center of an Au-coated four-turn square coil to generate ICPs, while different 13.56 MHz rf power was applied to the water cooled ( $25^\circ\text{C}$ ) substrate to induce bias voltages to the wafer. A 24-mm-thick quartz plate was used to separate the square coil from the plasma region. A square array of

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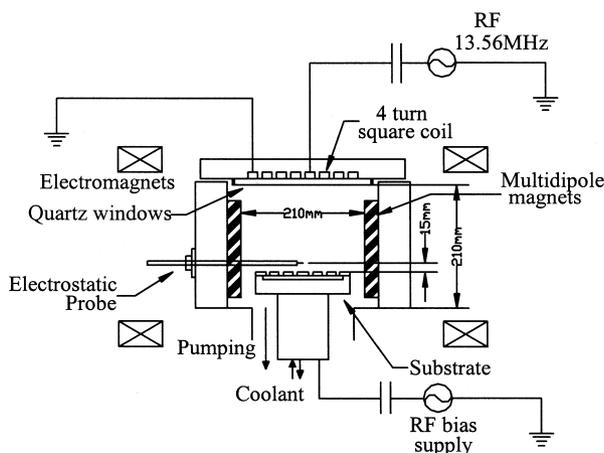


Fig. 1. Schematic diagram of the MICP etcher with Helmholtz type electromagnets and multidipole permanent magnets used in the experiment.

magnet housing made of anodized aluminum was installed inside of the chamber to hold permanent magnets having 3000 G on the magnet surface, and the magnets were arranged in the housings to form a magnetic cusp. For the magnetic cusping, 14 pairs of magnets were inserted in the anodized aluminum housings. A square (500 mm × 500 mm) shaped Helmholtz type axial electromagnets were also installed outside the chamber as shown in Fig. 1. More details of the system are described elsewhere [10].

Thin films of PZT (7000 Å thick) were deposited on Pt/Ti/Si substrates by a sol-gel process. The PZT films used in this experiment showed a perovskite phase when measured by X-ray diffraction. Etch rates were determined by stylus profilometry of feature depths after the removal of a 6.8- $\mu\text{m}$ -thick patterned photoresist.

To understand the effects of plasma conditions on the PZT etch properties, a quadrupole mass spectrometer (QMS; Hiden Analytical Inc. PSM 500) and a Langmuir probe (Hiden Analytical Inc., ESP) located on the sidewall chamber were used. Using the QMS, positive ion (e.g.  $\text{Cl}^+$  and  $\text{Cl}_2^+$ ) densities in the plasmas were measured by turning off the filament and by integrating collected ions having different ion energies. Scanning electron microscopy (SEM) was used to examine etch profiles.

### 3. Results and discussion

The application of Helmholtz type electromagnets to ICPs, therefore, the application of axial electromagnetic field to the plasmas, produces increased ionization and dissociation due to the increased power transfer to the plasmas [11]. However, the use of the axial

magnetic field generally decreases the uniformity of the plasmas along the radial direction. Therefore, to improve the uniformity, in addition to the Helmholtz type axial magnets, a magnetic bucket consisted of multiple permanent magnets described in Section 2 has been used and its effects on the plasma density and uniformity were investigated using a Langmuir probe. Fig. 2 shows the ion densities measured at 1.5 cm above the substrate along the radial direction from the center to the chamber wall for Ar plasmas. Ar plasmas were generated with 600 W of rf power and 5 mtorr of Ar pressure. The applied axial magnetic field by the electromagnet was 15 Gauss or 20 Gauss. As shown in the figure, the application of axial magnetic field increased the ion density and decreased the uniformity of the plasma along the radial direction compared to that by conventional non-magnetized ICP. However, when multidipole permanent magnets were applied around the chamber wall in addition to the Helmholtz type electromagnets, the increased ion density with increased uniformity of the plasma could be obtained. The increase of ion density and uniformity of the plasma by using multidipole magnets appears to be from the decrease of plasma loss to the chamber wall by the magnetic cusping used in the experiment [12,13].

PZT thin films were etched as a function of chlorine percentage in the  $\text{Cl}_2/\text{Ar}$  gas mixture using the conventional ICP and the magnetized ICP (MICP), magnetized both by Helmholtz electromagnets and multidipole permanent magnets. The other etch parameters such as rf power, bias voltage, and operational pressure were maintained the same as 600 W,  $-250$  V and 10 mtorr, respectively, and the etch results are shown in Fig. 3. In the figure, the etch selectivities over Pt are also shown. As shown in the figure, increased PZT etch

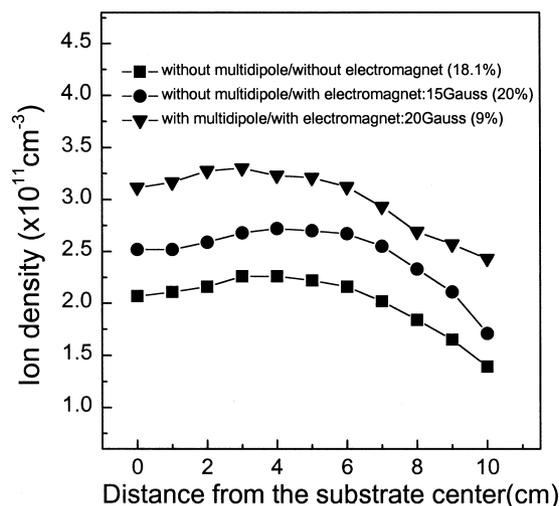


Fig. 2. Radial distribution of Ar ion density with/without the multidipole magnets and axial electromagnets at 5 mtorr of operational pressure and 600 W of inductive power.

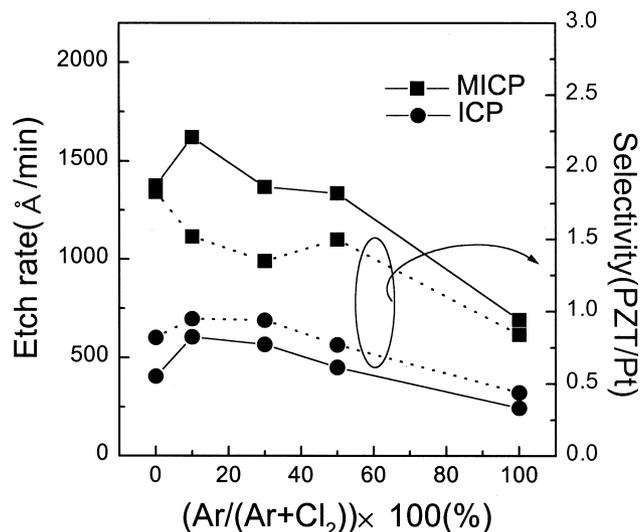


Fig. 3. PZT etch rates as a function  $\text{Cl}_2/\text{Ar}$  gas ratio for ICP and MICP. Process conditions: 600 W of inductive power,  $-250$  V of bias voltage, and 10 mtorr (30 sccm) of operation pressure.

rates and etch selectivities over Pt could be obtained by using MICP. However, the same highest etch rates were observed with 90%  $\text{Cl}_2/10\%$  Ar for both the conventional ICP and the MICP. A previous study showed approximately 1.7 times higher chlorine radical densities with the application of the magnetic cusping for the pure chlorine plasmas and also showed the highest chlorine radical densities with 90%  $\text{Cl}_2/10\%$  Ar in  $\text{Cl}_2/\text{Ar}$  plasmas [10,14]. Therefore, the increase of PZT etch rates with the application of the magnetic cusping in our experiment appears to be related to the increase of chlorine radical densities in the plasma.

In the case of PZT etching, in addition to the increased chlorine radical density described above, ion bombardment may be required to remove the chlorine compound from the etched surface due to the low volatility of the chlorine compounds such as  $\text{PbCl}_2$ ,  $\text{ZrCl}_4$ ,  $\text{TiCl}_4$ , etc. Therefore, ion densities in the chlorine-containing plasmas such as  $\text{Cl}_2^+$  and  $\text{Cl}^+$  were investigated as a function of ion energy using a QMS from both ICP and MICP, and the results are shown in Fig. 4a,b for  $\text{Cl}^+$  and  $\text{Cl}_2^+$ , respectively. The process condition used in the experiment was 90%  $\text{Cl}_2/10\%$  Ar, 600 W of rf power, and 10 mtorr of operational pressure. In Fig. 4a,b, the total number of  $\text{Cl}_2^+$  and  $\text{Cl}^+$  ions detected using the QMS are also shown in addition to the their energy distribution. As shown in the figure, the number of  $\text{Cl}^+$  ions detected for MICP were similar to those detected for conventional ICP, however, the ions for MICP were distributed at lower energies by approximately 5 eV. In the case of  $\text{Cl}_2^+$ , the number of ions detected for MICP was increased approximately 2.5 times compared with those for conven-

tional ICP and the ion energy distribution was shifted to lower energy of approximately 5 eV similar to  $\text{Cl}^+$ . If the ratio of  $\text{Cl}_2^+/\text{Cl}^+$  is compared, the application of the magnets increased the ratio of  $\text{Cl}_2^+/\text{Cl}^+$  increased from 1.7 to 3.9 for the same process gas mixture. The increased  $\text{Cl}_2^+$  ions in the plasma will increase both the chemical and/or physical sputtering effect and the chemical reactivity for the PZT etching. Therefore, in the PZT etching of our experiment, the use of our magnetic configuration increases both reactive Cl radicals and  $\text{Cl}_2^+$  ions, and their increased chemical reactivity and chemical and/or physical sputtering effects appear to increase the PZT etch rates and possibly the etch selectivity, too. The lower energy distribution of the ions observed for both  $\text{Cl}_2^+$  and  $\text{Cl}^+$  with MICP is related to the lower plasma potential of the plasma. In fact, when the plasma potentials of the plasmas were measured using a Langmuir probe, lower plasma potentials were measured for MICP compared with those

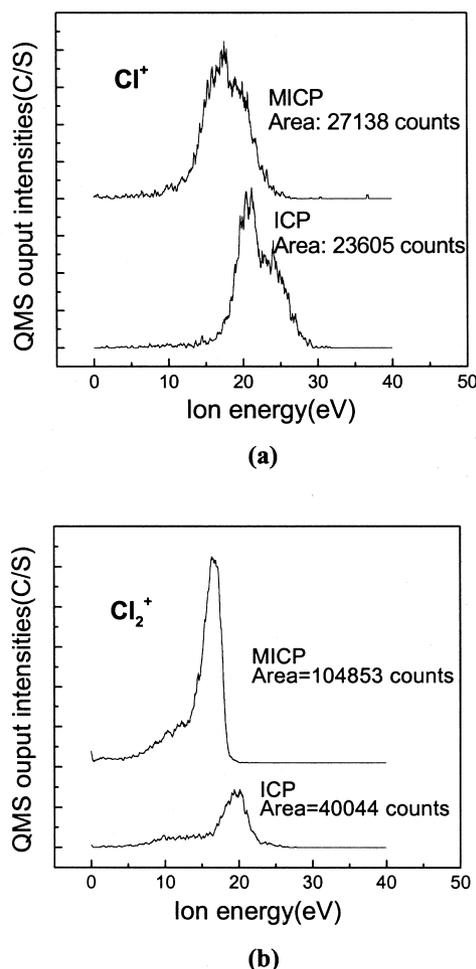


Fig. 4. Ion energy distribution of (a)  $\text{Cl}^+$  and (b)  $\text{Cl}_2^+$  in 90%  $\text{Cl}_2/10\%$  Ar for ICP and MICP measured by QMS on the sidewall of the chamber. Process conditions: 600 W of inductive power and 10 mtorr (30 sccm) of operation pressure.

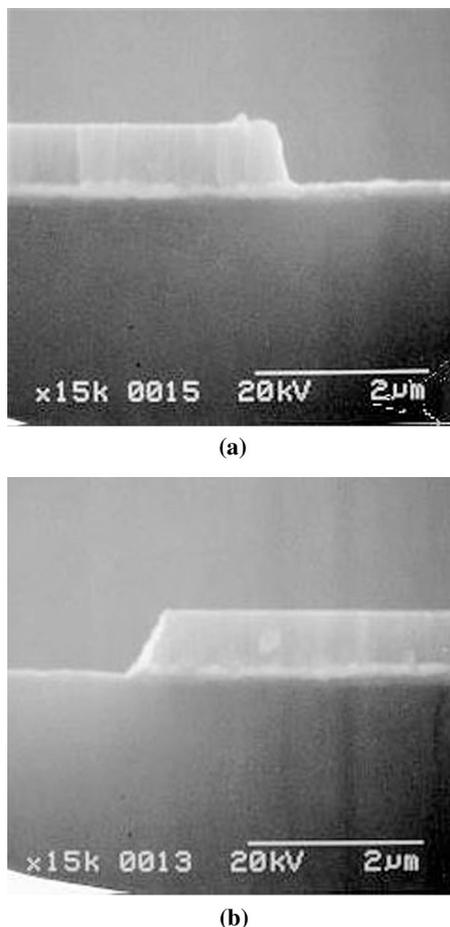


Fig. 5. Typical etch profiles of PZT thin films with (a) ICP and (b) MICP in the 90%  $\text{Cl}_2$ /10% Ar gas mixture. Process conditions: 600 W of inductive power,  $-250$  V of bias voltage and 10 mtorr (30 sccm) of operation pressure.

for conventional ICP [10]. The lower plasma potentials obtained with MICP will reduce possible contaminations from the chamber wall.

Using the MICP and the conventional ICP, 7000-Å-thick PZT thin films patterned using a photoresist were etched at the condition of 90%  $\text{Cl}_2$ /10% Ar, 600 W of rf power, 10 mtorr of operational pressure, and  $-250$  V of dc self-bias voltage and their etch profiles were observed using SEM. The etch profiles are shown in Fig. 5a for the conventional ICP and Fig. 5b for the MICP. As shown in the figure, more anisotropic PZT etch profile was obtained with MICP possibly due to the increased chemical and physical sputtering of the low vapor pressure chlorine compounds which could be accumulated on the sidewall of the etched surface and reduce the anisotropy of etch profiles.

#### 4. Conclusions

In this study, PZT thin films were etched using

conventional ICPs and MICPs by both Helmholtz type electromagnets and multidipole permanent magnets, and their etch characteristics and plasma characteristics were compared.

The use of Helmholtz type magnets to the conventional ICP increased the ion density, however, it decreased the uniformity of the plasma. The increase of ion density with the increased uniformity of the plasma could be obtained using both the Helmholtz type electromagnets and multidipole permanent magnets around the chamber wall. When the PZT thin films were etched using the MICP which consisted of Helmholtz type electromagnets and multidipole magnets, higher PZT etch rates and etch selectivities over Pt could be obtained when compared with those by conventional ICP. Also, more anisotropic etch profiles were obtained with the MICP. The increased PZT etch rates and etch selectivities over Pt with MICP appear to be related to increased chemical reactivity and physical sputtering effect by the increased Cl radicals and  $\text{Cl}_2^+$  ion densities with the magnetic confinement used in our experiment.

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