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Comparison of chlorine- and fluorine-based inductively coupled plasmas for the dry etching of PZT films

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A comparative study on the etch rate and surface morphology of PZT films and etch selectivity for PZT over Pt has been conducted in chlorine- (Cl_2 and BCl_3) and fluorine (CF_4 and SF_6)-based inductively coupled plasmas. The PZT etch rate, surface morphology and etch selectivity for PZT over Pt films are a strong function of plasma composition, ion flux and ion energy in both chemistries. Chlorine-based inductively coupled plasmas produced higher etch rates for PZT (max. ~3500 Å/minute) while fluorine-based plasmas showed higher etch rates (max. ~1800 Å/minute) for the Pt film. The maximum etch selectivity ~4.5 for PZT over Pt was obtained at a relatively high source power (900 W) and moderate RF chuck power (250 W) condition.

Key words: lead zirconate titanate (PZT), inductively coupled plasma etching, chlorine- and fluorine-based plasmas, high rate dry etching of PZT, etch selectivity for PZT/Pt .

Introduction

Lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$, PZT), a perovskite structure ceramic material, is one of the most prominent and useful electroceramics and has attracted much attention due to its excellent ferroelectric, dielectric, pyroelectric and piezoelectric properties. PZT has been used as a bulk material in numerous ultrasound transducers, sensors, high-value ceramic capacitors, and ceramic resonators [1-5]. PZT thin films which have a composition near x = 0.52 feature an extremely large dielectric constant as well as bistable polarization characteristics and they have been used in non-volatile ferroelectric random access memories (FRAM) [6-8].

In the mean time, the superior piezoelectric properties of PZT thin films encourage their wide use as electromechanical transducer layers for sensors and actuators in micro-electromechanical systems (MEMS). In particular, PZT thin film-based micro-cantilevers are being considered not only to achieve a reduction effect in the size of the whole system but also to realize sensors with high sensitivity due to their larger electrostrictive strain than ZnO and AlN when resonance occurs [9-12].

There are two critical technological issues in the fabrication of a piezoelectric micro-cantilever and actuators which typically consists of a Pt/PZT (0.5-2 μm)/Pt multilayer. One is dry etch patterning of PZT and Pt films with a high rate for the micrometre scale patterning of the actuating part. The other is a high etch selectivity for PZT over Pt which is required for the efficient bottom electrode opening. Lee *et al.* reported that magnetized inductively coupled plasmas (MICP) of Cl_2/Ar increased the PZT etch rates up to 170 nm/minute, three times higher than for conventional ICP plasmas [13]. Baborowski *et al.* suggested optimized electron cyclotron resonance (ECR) etching conditions where practical etch rates ~60 nm/minute, sufficient anisotropy, etch selectivity ~1.5 for PZT over Pt, and residue-free patterning could be achieved [14]. An *et al.* presented higher PZT etch rates (max. ~245 nm/minute) in planar inductively coupled BCl_3/Cl_2/Ar plasmas, but the etching was performed at an elevated temperature of 80 °C [15]. In spite of much research effort which has been made previously, achieving a high etch rate of PZT and an adequate etch selectivity for PZT/electrode seems still to remain as a technical obstacle [16-18]. In this paper, we report a comparative study on the etch characteristics of PZT and Pt films in chlorine- and fluorine-based ICP discharges. The PZT etch rates and etch selectivity for PZT over Pt film were generally higher with chlorine-based inductively coupled plasmas. Chlorine-based ICP discharges were found to be very useful chemistries that allow a full range of the desired etching properties in the fabrication of PZT-based piezoelectric micro-cantilever and actuators, i.e., nonselective and selective for PZT over Pt.

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Experimental

~6000 Å thick PZT thin films were deposited on Si substrates by an RF magnetron sputtering technique using a sintered ϕ3" (75 mm) PZT disk with a composition near the morphotropic boundary of Zr/Ti = 0.53/0.47 as the sputtering target. Excessive PbO was also included in the target to compensate for the volatilization of Pb during deposition or subsequent annealing. The substrate temperature and chamber pressure were fixed at 300 °C and 2×10^{-2} Torr (2.67 Pa) during deposition in argon-oxygen gas mixtures. As-deposited PZT films were annealed at 650 °C for 2 h in order to crystallize them into a perovskite structure. Pt films with a thickness of ~3000 Å were deposited on Si substrates by an e-beam evaporation process at a process pressure of 1×10^{-5} Torr (1.33×10^{-3} Pa). PZT and Pt films were patterned with various mask materials, including photoresist and SiN_x. High density plasma etching was performed in a planar inductively coupled plasma source operating at 13.56 MHz and with a power up to 1000 W, and the samples were thermally bonded to a Si carrier wafer that was mechanically clamped to a He backside-cooled, RF-powered (13.56 MHz, up to 450 W) chuck. Chlorine- (Cl_2/Ar and BCl_3/Ar) or fluorine-(CF_4/Ar and SF_6/Ar) inductively coupled plasmas were employed to etch PZT and Pt wafers, and the total gas load was fixed at 15 standard cubic centimeters per minute (sccm). After removal of the mask the material etch rate, surface morphology and near-surface stoichiometry were characterized by stylus profilometry measurements, scanning electron microscopy (SEM), atomic force microscopy (AFM) and Auger electron spectroscopy (AES).

Results and Discussion

Fig. 1 shows the plasma composition dependence of the PZT etch rate in both the chlorine- (Cl_2/Ar and BCl_3/Ar, top) and fluorine- (CF_4/Ar and SF_6/Ar, bottom) based ICP discharges at a fixed source power (750 W), RF chuck power (250 W) and pressure (0.267 Pa). Two noticeable things are observed from these results. Firstly, chlorine-based ICP plasmas produce a higher etch rate from PZT than with fluorine-based discharges and this can be readily understood by considering the volatility of metal chloride and metal fluoride etch products. The boiling points of the potential etch products of PZT with chlorine- or fluorine-based plasmas are presented in Table 1 [19]. As shown in Table 1, most of the metal chloride etch products (presumably $PbCl_2$, $PbCl_4$, $ZrCl_4$ and $TiCl_4$) are more volatile than the metal fluoride etch products (presumably PbF_4, ZrF_4, and TiF_3), which leads to the higher PZT etch rates in chlorine-based ICP plasmas than with CF_4 or SF_6 discharges. Secondly, higher PZT etch rates were obtained with Cl_2/Ar or SF_6/Ar ICP plasmas than with BCl_3/Ar or CF_4/Ar plasmas under the same conditions. In high density plasma etching, the etch rate is generally determined by the etch product formation and subsequent ion-assisted removal of the

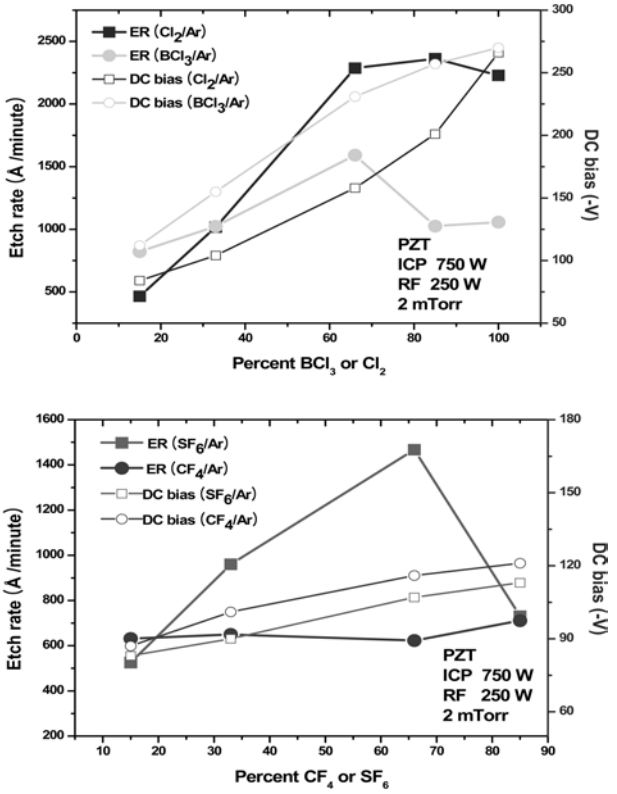

Fig. 1. PZT etch rates as a function of plasma composition in both chlorine- (top) and fluorine-based (bottom) ICP discharges (750 W source power, 250 W RF chuck power, 0.267 Pa).

Table 1. Boiling points of potential etch products of PZT with chlorine- or fluorine-based plasmas.

Product	Boiling point (°C)	Product	Boiling point (°C)	Product	Boiling point (°C)
$PbCl_2$	951	$ZrCl_2$	1292	$TiCl_2$	1500
$PbCl_4$	50	$ZrCl_4$	331	$TiCl_4$	136.5
PbF_4	1293	ZrF_4	913	TiF_3	1400

resultant etch products, and etch product formation is limited by the supply of the reactive neutral species to the surface [20-22]. By taking account of a collision-cascade model [23, 24], Cl_2 and SF_6 gases are expected to supply higher densities of reactive chlorine or fluorine radicals to the surface than BCl_3 and CF_4 gases under the same conditions, resulting in the enhanced etch product formation (compare the average molar bond energies of each gases; Cl_2 : 240 kJ/mol, BCl_3 : 456 kJ/mol, SF_6 : 284 kJ/mol, and CF_4 : 485 kJ/mol) [25].

In Fig. 2, the effect of ICP source power on the PZT etch rates at fixed plasma compositions and RF chuck power is presented. For Cl_2/Ar discharges, the PZT etch rate increases monotonically as the source power increases due to the enhanced dissociation of the discharges and reaches a max. ~3500 Å/minute, the highest etch rate ever reported. For BCl_3/Ar and fluorine-based plasma chemistries, the PZT etch rate initially increases as the source power

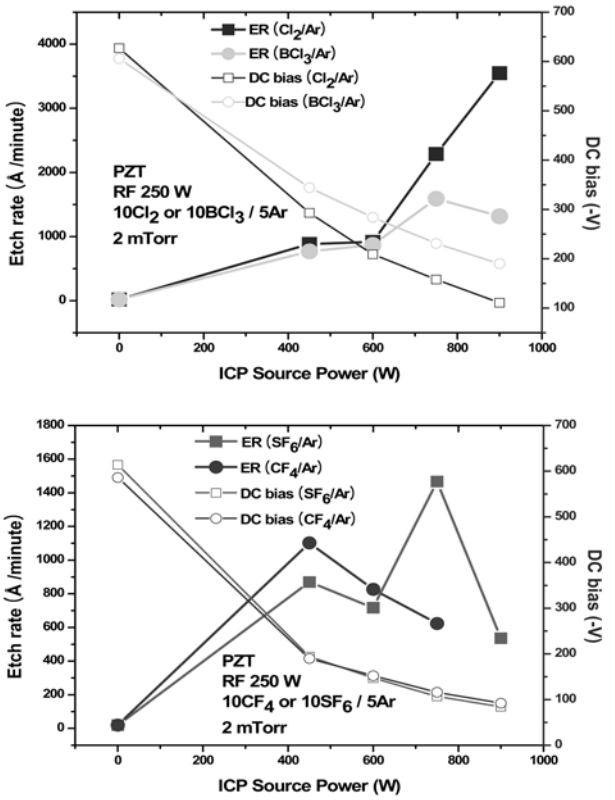

Fig. 2. PZT etch rates as a function of source power in both chlorine- (top) and fluorine-based (bottom) ICP discharges (250 W RF chuck power, 0.267 Pa).

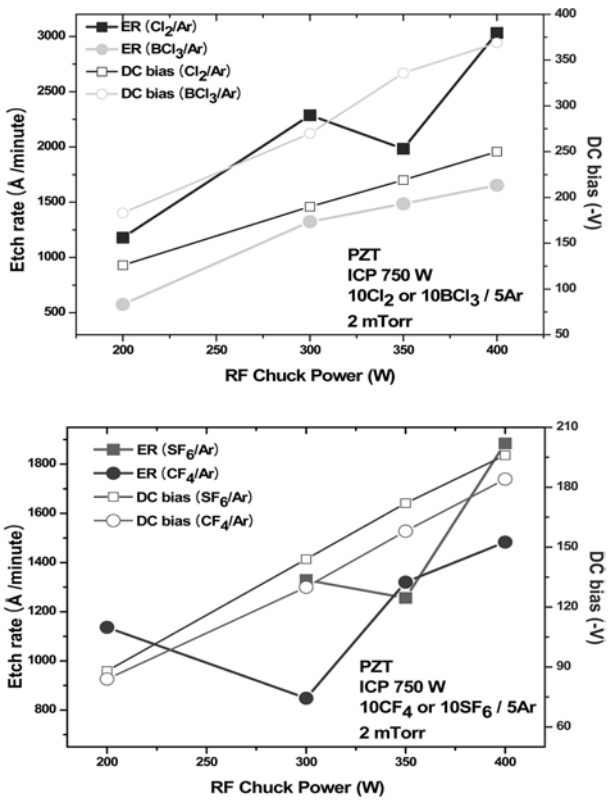

Fig. 3. PZT etch rates as a function of RF chuck power in both chlorine- (top) and fluorine-based (bottom) ICP discharges (750 W source power, 0.267 Pa).

increases, but then decreases beyond particular source powers. This is consistent with an etch mechanism in which the etch products formed by the chemical reaction between the component elements of the PZT film and the adsorbed chlorine or fluorine neutrals should be balanced with ion-assisted desorption. Beyond the optimum source powers, the ion flux keeps increasing, but the average ion energy in the plasma falls down below that needed to efficiently remove metal chloride or metal fluoride etch products from the surface. Therefore, the etching would be limited by ion-assisted desorption.

The dependence of PZT etch rates on RF chuck power is shown in Fig. 3 for chlorine-based (top) and fluorine-based ICP discharges (bottom) at a fixed source power (750 W) and pressure (0.267 Pa). For chlorine-based and SF_6/Ar plasma chemistries the PZT etch rates are strongly dependent on the RF chuck power due to the enhanced ion-assisted desorption of metal chloride or metal fluoride etch products. The PZT etch rates fall off at relatively higher power conditions (300-350 W), which is ascribed to the ion-assisted sputtering of the reactive chlorine or fluorine radicals before they have a chance to complete a reaction with substrate atoms. Maximum etch rates ~3000 Å/minute and ~1900 Å/minute are obtained in Cl_2/Ar and SF_6/Ar ICP plasmas, respectively.

Fig. 4 shows the normalized roughness values of PZT surfaces etched in both chlorine-based (top) and fluorine-

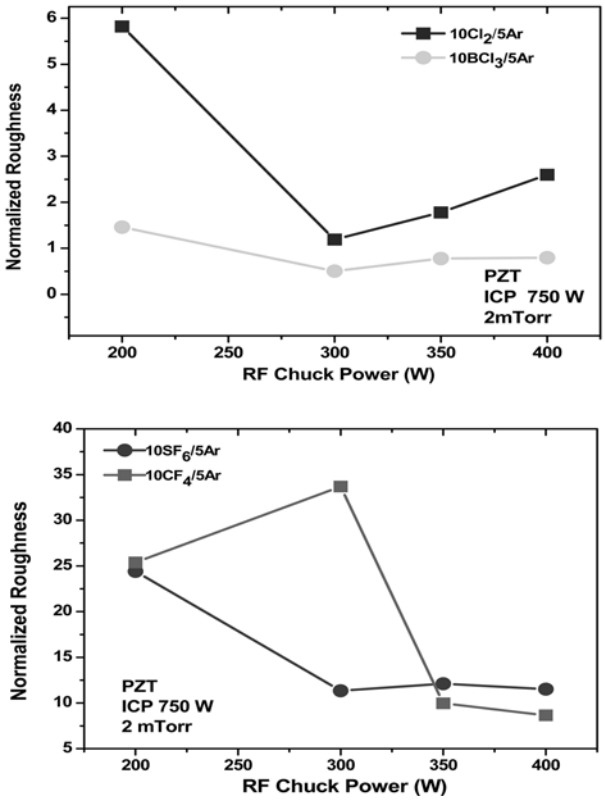

Fig. 4. Dependence of PZT normalized etched surface roughness on RF chuck power in both chlorine- (top) and fluorine-based (bottom) ICP discharges (750 W source power, 0.267 Pa).

based ICP discharges (bottom) as a function of RF chuck power at a fixed plasma composition and source power. The PZT samples etched in BCl_3/Ar ICP discharges show similar or better root-mean-square (RMS) roughness values than the unetched control sample (RMS roughness: 2.068 nm) while degradation in surface morphology to some extent was observed after etching in Cl_2/Ar ICP discharges. By contrast, a severe degradation in surface morphology occurred after etching in fluorine-based ICP discharges. A consistent smoothing of the surface was observed at higher RF power conditions, most likely due to the activated ion-enhanced removal of metal fluoride etch products or sharp features from the surface. As shown in Fig. 1 to Fig. 3, although BCl_3/Ar plasmas produced lower etch rates than Cl_2/Ar discharges under most of the conditions examined, but BCl_3/Ar ICP etching is thought to be an attractive choice if a smooth surface finish is needed.

Fig. 5 presents the AES surface scans of the unetched PZT control sample (top) and a PZT film etched in $10Cl_2$/5Ar ICP discharges (bottom) with a 600 W source power, 250 W RF chuck power and 0.267 Pa pressure condition. The near surface stoichiometry of PZT film was found not to be significantly affected by the Cl_2/Ar ICP etching since the relative fraction of each component element in the top ~20 nm of the etched PZT film remained similar to that of the unetched control samples.

The ICP source power dependence of the Pt etch rate (top) and the resultant etch selectivity for PZT over Pt films (bottom) in Cl_2/Ar and BCl_3/Ar discharges are shown in Fig. 6. The Pt etch rate increases almost linearly up to a moderate source power and then a further increase in the source power does not produce a significant increase in etch rate since a selvedge layer involving the less volatile $PtCl_x$ etch products may form on the surface, which is not removed efficiently under the reduced ion energy available. Under the same conditions, the PZT etch rate is strongly dependent on the source power as shown in Fig. 2 and the maximum etch selectivity ~4.5 for PZT over Pt is obtained in Cl_2/Ar ICP plasmas at a high source power and a moderate RF chuck power condition. For SF_6/Ar discharges, the maximum etch selectivity for Pt over PZT as high as a maximum ~2.0 was obtained due to the high volatility of PtF_x etch products (presumably PtF_6 : boiling point 69.1 °C).

Summary and Conclusions

The effects of plasma composition, source power and RF chuck power on the PZT etch rate and etch selectivity for PZT over Pt were examined in Cl_2-, BCl_3-, CF_4-, and SF_6-based inductively coupled plasmas. Higher PZT etch rates were achieved with Cl_2- and BCl_3-based ICP discharges than with CF_4/Ar and SF_6/Ar mixtures due to the higher volatility of metal chloride etch products. Cl_2/Ar or SF_6/Ar ICP plasmas produced higher PZT etch rates than BCl_3/Ar or CF_4/Ar plasmas since Cl_2 and SF_6 gases appear to supply higher densities of reactive chlorine or fluorine

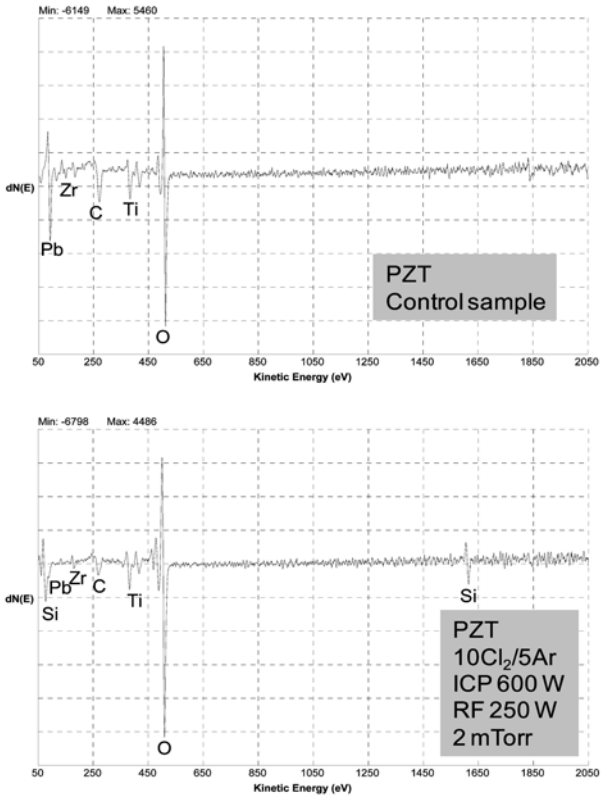

Fig. 5. AES surface scans of the unetched (top) and etched (bottom) PZT films in $10Cl_2$/5Ar ICP discharges (600 W source power, 250 W RF chuck power, 0.267 Pa).

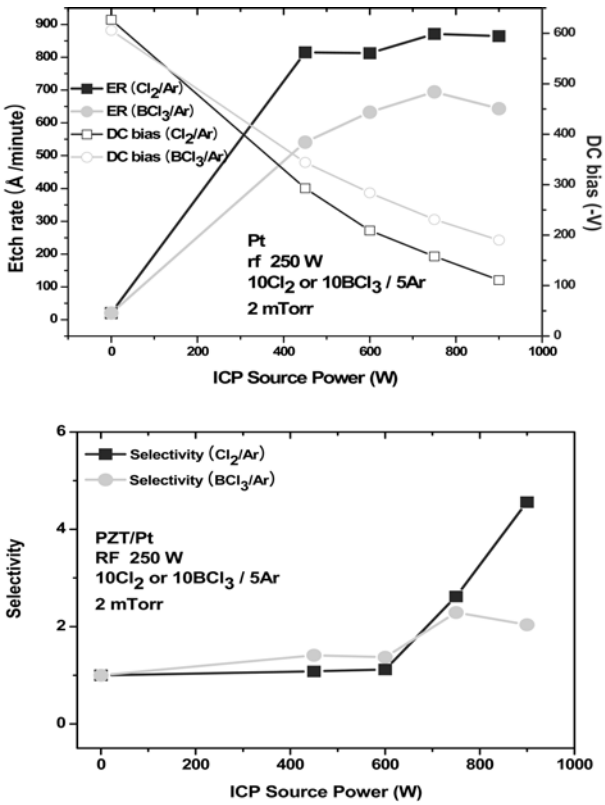

Fig. 6. Pt etch rates (top) and etch selectivity for PZT over Pt (bottom) as a function of source power in chlorine-based ICP discharges (250 W RF chuck power, 0.267 Pa).

radicals to the surface, which leads to an enhanced etch product formation. A maximum etch rate ~3500 Å/minute, the highest PZT etch rate ever reported, was obtained in Cl_2/Ar ICP discharges while BCl_3/Ar mixtures were found to provide smooth surface morphologies. Cl_2/Ar ICP plasmas produced a maximum etch selectivity ~4.5 for PZT over Pt at a high source power and a moderate RF chuck power condition, while a maximum etch selectivity in reverse ~2.0 was achieved with SF_6/Ar discharges due to the high volatility of PtF_x etch products. Chlorine- and fluorine-based inductively coupled plasma etch processes seem to be very applicable to PZT-based piezoelectric microactuator and microcantilever fabrication.

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