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# Dry Etching of $SrBi_2Ta_2O_9$: Comparison of Inductively Coupled Plasma Chemistries

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Abstract−A systematic study of the etch characteristics of $SrBi_2Ta_2O_9$ (SBT) thin films in inductively coupled plasmas (ICPs) has been performed with various chemistries of $Cl_2/Ar$, $Cl_2/O_2/Ar$, $Cl_2/NF_3/Ar$, and $Cl_2/NF_3/O_2/Ar$. Etch rate was dependent on plasma chemistries and parameters. Addition of $O_2$ stabilized the perovskite structure of SBT film and suppressed the etch rate, but $NF_3$ enhanced the etch rate substantially mainly due to reactive fluorine radicals. Maximum etch rates obtained were: 740 Å/min with $Cl_2/Ar$, 320 Å/min with $Cl_2/O_2/Ar$, 1,500 Å/min with $Cl_2/NF_3/Ar$, and 1,600 Å/min with $Cl_2/NF_3/O_2/Ar$ at 5 mTorr, 700 W ICP power and 150 W rf chuck power. Electrical properties of the SBT films were quite dependent on plasma chemistries employed; $Cl_2/NF_3/O_2/Ar$ showed the least damage in the films and resulted in the best P-E hysteresis loop having remnant polarization ($2P_r$)=12.3 μC/cm$^2$ and coercive field ($E_c$)=41.9 V/cm.

Key words: Dry Etching, SBT($SrBi_2Ta_2O_9$), ICPs

## INTRODUCTION

Recently, a ferroelectric random access memory (FRAM) device, called a non-volatile memory for next generation, has received much attention because it retains information when power is interrupted. The FRAM devices require low operating voltage, fast switching speed, wide operating temperature range, and high radiation hardness [Lee et al., 1996, 1999; Park et al., 1999]. For the FRAMs application, ferroelectric materials such as $Pb(Zr, Ti)O_3$ and Bi-layered structure oxides have been studied intensively. Among these, the Bi-layered perovskite $SrBi_2Ta_2O_9$ (SBT) is known as a promising candidate for FRAM applications due to its excellent properties such as a high fatigue resistance against polarization switching up to $10^{12}$ cycles [Bu et al., 1999; Park et al., 1999]. Dry etching of the ferroelectric thin films is an important issue for pattern transfer in the fabrication of FRAM devices.

In recent years, the most significant advancement in dry etching of semiconductor materials has been the utilization of high-density plasmas. The majority of the high-density plasma etching has been performed by using inductively coupled plasma (ICP) etch systems because of their superior uniformity, control, and lower cost of ownership [Shul et al., 1997; Hahn et al., 1999; Hahn and Pearton, 2000]. There are a few studies reported on the etch characteristics of SBT films, but little work has been done in terms of plasma chemistries.

Desu and Pan in 1996 reported the etching characteristics of SBT and $SrBi_2Ta_xNb_{2-x}O_9$ films using $SF_6$ and $CHClFCF_3$ in a capacitively coupled plasma reactive ion etching (RIE) system, and obtained an etch rate of <200 Å/min. Lee et al. in 1999 investigated etching behavior and damage recovery of SBT films in a magnetron-enhanced reactive ion etching system using $Ar/CF_4/O_2/Cl_2$ plasmas. They also reported relatively slow etch rate (<280 Å/min) at about 65 °C and substantial damage of etched samples, resulting in poor electrical properties. Im et al. in 2001 first reported an etch rate of 1,500 Å/min with $Cl_2/NF_3/Ar$ at 55 °C and moderate ICP conditions.

In this article, we report the etch characteristics of $SrBi_2Ta_2O_9$ thin films with different plasma chemistries of $Cl_2/Ar$, $Cl_2/O_2/Ar$, $Cl_2/NF_3/Ar$, and $Cl_2/NF_3/O_2/Ar$, carried out in a planar-type inductively coupled plasma etcher. The influences of plasma chemistries and plasma parameters have been analyzed in terms of the etch rate, the surface roughness, and the polarization-electric field (P-E) loops. $Cl_2/NF_3/O_2/Ar$ was found to be a very promising chemistry that allows practical etch rate, smooth surface, and good electrical property.

## EXPERIMENTAL

The SBT films were prepared on Pt(1,500 Å)/Ti(500 Å)/$SiO_2$/Si substrates by using a radio frequency (rf) sputtering system equipped with a planar magnetron sputtering source. A planar-type Vacuum Science ICP system (VSICP-1250A), in which the ICP source operated at 13.56 MHz, was used to etch as-grown SBT films. The ICP etcher was pumped out by a turbomolecular pump up to $10^{-7}$ Torr and the operating pressure (ranged 5 to 50 mTorr) was controlled by a throttle valve at fixed gas flow rates. The temperature of the SBT substrate in the ICP etcher, sitting on the backside-cooled sample chuck (or the bottom electrode), was held at about 55 °C. The etch gas was injected into the ICP etcher through electronic mass flow controllers (MFCs). The ion energy was controlled by the applied rf chuck power at 13.56 MHz. For the etch rate experiments, samples (4 mm×4 mm) were masked with Apiezon wax. Etch depths were obtained from stylus profilometry measurements of the etched samples after removal of the wax. The crystalline structure and surface morphology were analyzed using x-ray diffraction (XRD) patterns and atomic force microscope (AFM), respectively.

Electrical characterization of the films was performed by using a Pt/SBT/Pt capacitor structure in terms of the polarization-electric

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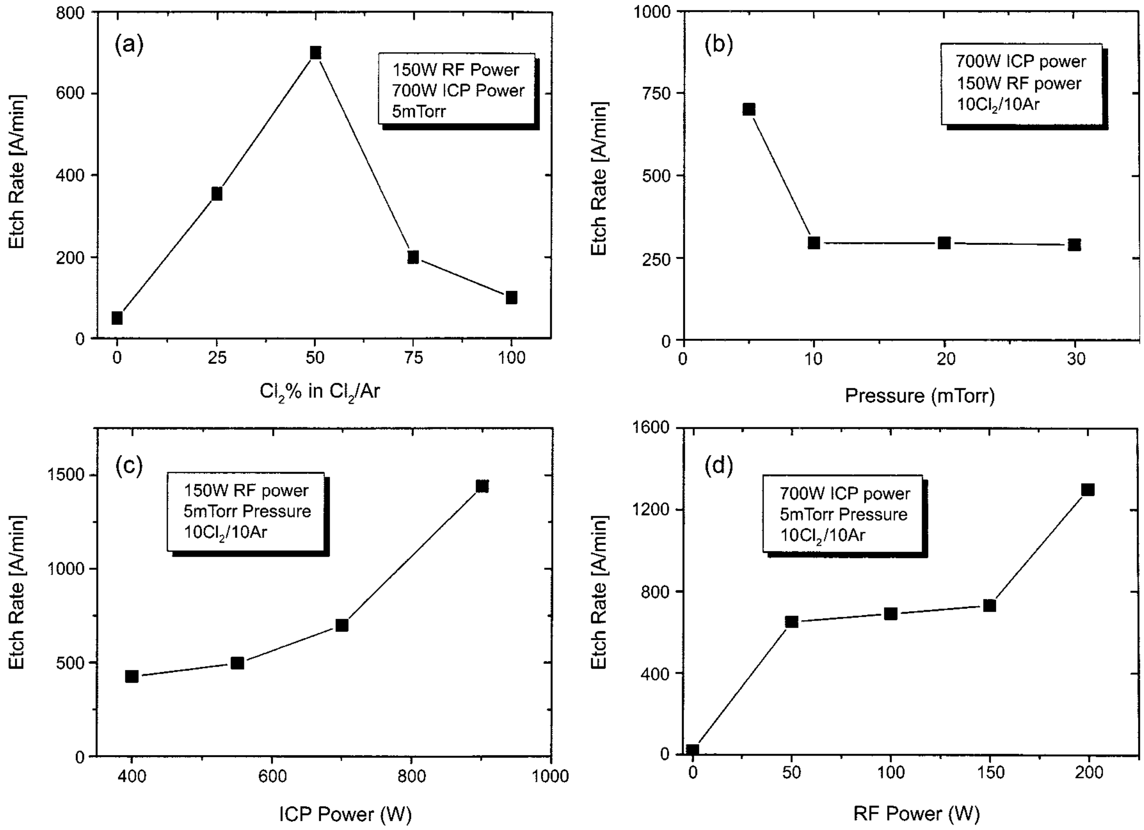


**Fig. 1. Effects of (a) $Cl_2$ concentration, (b) pressure, (c) ICP source power, and (d) rf chuck power on the etch rate of SBT film in $Cl_2$/Ar plasma.**

(P-E) field hysteresis loop. For the Pt/SBT/Pt capacitor, platinum top electrode (1 mm in diameter) was deposited by a dc magnetron sputtering system. The Pt top layer was also used as a mask layer for the fabrication of the Pt/SBT/Pt capacitor.

## RESULTS AND DISCUSSION

Fig. 1 shows the effects of $Cl_2$ concentration, pressure, ICP source power, and radio frequency (rf) chuck power on the etch rate of SBT film in $Cl_2$/Ar discharges. The etch rate showed a maximum value (740 Å/min) at 50% $Cl_2$ and decreased beyond 50% [Fig. 1(a)]. The decrease in etch rate at higher chlorine contents can be attributed to the fact that additional collisional energy losses are present with increasing $Cl_2$ concentration. Compared to pure Ar discharges, $Cl_2$/Ar chemistry induces a decrease in ion flux at higher $Cl_2$ concentration because additional energy losses are caused by excitation of vibrational and rotational energy levels, molecular dissociation and negative ion formation [Lieberman and Lichtenberg, 1994]. This energy loss results in less formation of ions in bulk plasma and thus decrease in etch rate at higher $Cl_2$ concentration.

The etch rate was decreased at 10 mTorr and remained almost constant beyond 10 mTorr [Fig. 1(b)]. It is known that concentration of neutrals increases with increasing pressure, but at the same time the recombination rate of ions and electrons in the bulk plasma also increases with pressure [Lieberman and Lichtenberg, 1994]. The increase in recombination rate then produces less incident ions onto the wafer surface, resulting in less effect of physical sputtering on removal of etch products. Hence, one may conclude that the dry etching of the SBT film is dominated by physical sputtering at lower pressures mainly due to less recombination of ions and longer mean free path of ions.

Fig. 1 also shows that the etch rate increases with increasing the ICP source power (c) and the rf chuck power (d). This result is attributed to the fact that etch rate is enhanced with an increase in incident ion flux onto the substrate with increasing the ICP source power, and with sputter desorption of etch products as the ion energy (or rf chuck power) increases. In a dry etching using a plasma, the role of ions is critical for anisotropic etch profiles because physical bombardment (or sputtering) activates the wafer surface and thus enhances chemical etching, resulting in a vertical depth profile. Our results clearly showed that the etch rate of SBT films increased with the rf chuck power and with the ICP source power. By contrast, we obtained a very slow etch rate with pure argon plasma [Fig. 1(a)] and no etch rate without applying the rf chuck power [Fig. 1(d)]. These lead to the conclusion that an energetic ion-assisted chemical etching is the dominant mechanism for SBT films in the ICP etcher. It is also worthwhile to see that fast etch rates of 1,500 Å/min and 1,300 Å/min were obtained at 900 W ICP [Fig. 1(c)] and at 200 W rf power [Fig. 1(d)], respectively. However, they resulted in worse crystal structure and electrical property because of plasma damage.

Fig. 2 illustrates the effect of oxygen addition to $Cl_2$/Ar on the etch rate of SBT in terms of $O_2$ concentration (a), pressure (b), ICP source power (c), and rf chuck power (d). The most significant dif-

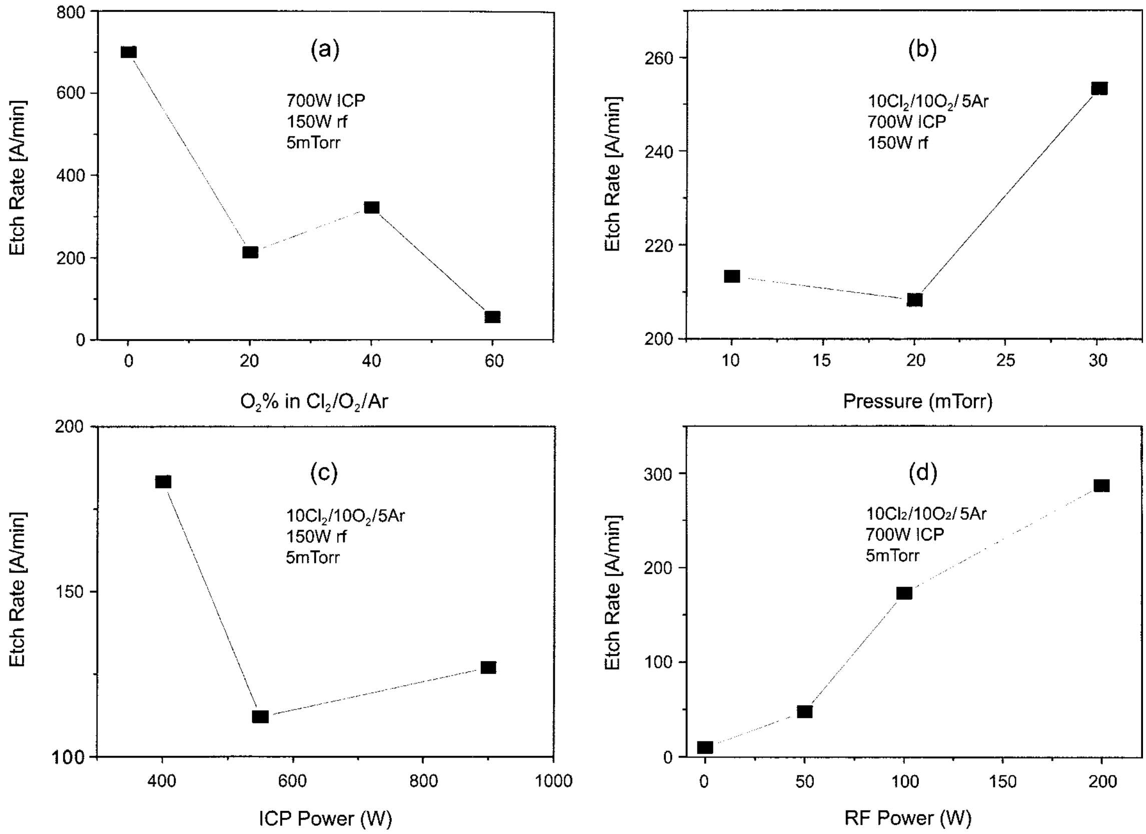


**Fig. 2. Effect of (a) $O_2$ concentration, (b) pressure, (c) ICP source power, and (d) rf chuck on the etch rate of SBT film in $Cl_2/O_2/Ar$ plasma.**

ference from the $Cl_2/Ar$ ICP etching is that the etch rate (50-320 Å/min) with $Cl_2/O_2/Ar$ is much slower than that with $Cl_2/Ar$. This result indicates that the addition of oxygen may compensate oxygen deficiency and stabilize the film chemically by sustaining the perovskite layers, thus leading to a slow etch rate.

In order to obtain higher etch rate at moderate etch conditions (700 W, 150 W, and 5 mTorr), we examined fluorine-containing etch gases such as $Cl_2/NF_3/Ar$ and $Cl_2/NF_3/O_2/Ar$. Fig. 3 shows the effect of addition of $NF_3$ to $Cl_2/Ar$ plasma on the etch rate and the dc-bias voltage (or the ion energy). Compared to the $Cl_2/Ar$ plasma, $Cl_2/NF_3/Ar$ resulted in faster etch rate of 1,450-2,200 Å/min, depending on $NF_3$ concentration. This is attributed mainly to the introduction of reactive fluorine radicals. It is also interesting to see that the dc bias somewhat increased with increasing the $NF_3$ percentage, indicating less formation of ions.

To understand the effect of oxygen addition, $Cl_2/NF_3/O_2/Ar$ plasma was utilized and results are shown in Fig. 4. Compared to the $NF_3/O_2/Ar$ plasma, $Cl_2/NF_3/O_2/Ar$ showed much slower etch rates, but faster rates than those with $Cl_2/Ar$. This is attributed to the same reason as in the case of oxygen addition to $Cl_2/Ar$. Hence, we conclude that presences of fluorine and oxygen in $Cl_2$-based plasma are crucial for obtaining faster etch rate and less damage of the etched

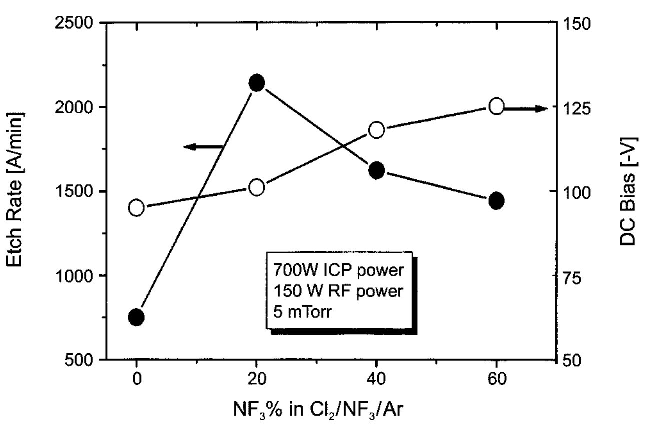


**Fig. 3. Effect of $NF_3$ concentration in $Cl_2/NF_3/Ar$ plasma on the etch rate of SBT film (700 W ICP, 150 W rf, and 5 mTorr).**

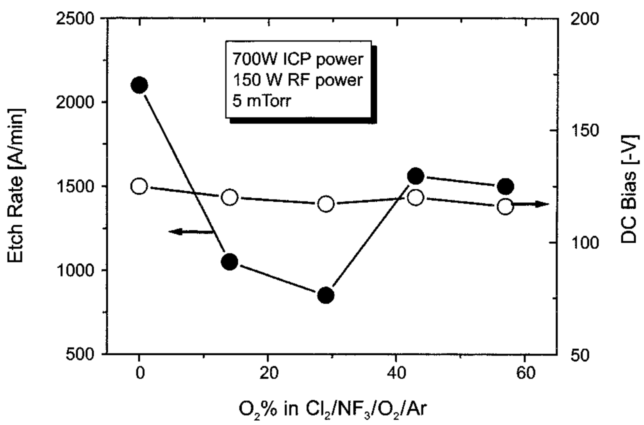


**Fig. 4. Effect of $O_2$ concentration in $Cl_2/NF_3/O_2/Ar$ plasma on the etch rate of SBT film (700 W ICP, 150 W rf, and 5 mTorr).**

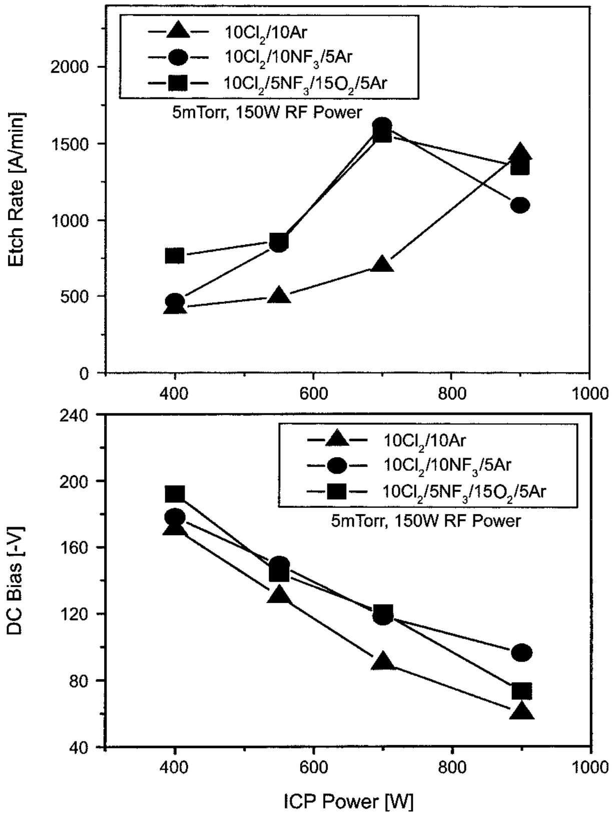


**Fig. 5. Effect of ICP source power on etch rate of SBT film with $Cl_2/NF_3/Ar$ and $Cl_2/NF_3/O_2/Ar$ (150 W rf and 5 mTorr).**

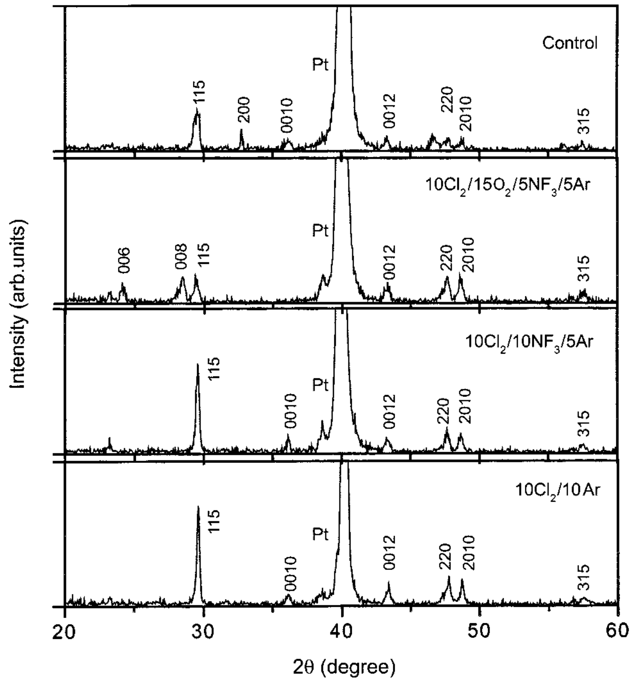


**Fig. 6. XRD patterns of control and SBT films etched with different plasma chemistries (700 W ICP, 150 W rf, and 5 mTorr).**

SBT films, respectively.

Fig. 5 shows the effect of the ICP source power on etch rates of SBT films and dc bias in $Cl_2/Ar$, $Cl_2/NF_3/Ar$ and $Cl_2/NF_3/O_2/Ar$ plasmas. During these experiments, the reactor pressure and the rf chuck power were held constant at 5 mTorr and 150 W. Both chemistries showed almost the same trend, and maximum etch rates of 1,500-1,600 Å/min at 700 W. They also showed substantial decreases in the dc bias with increasing the ICP source power, mainly due to the increased ion density at a higher ICP power. The increase in the etch rate is attributed to an ion-assisted etch mechanism. However, the decrease in etch rate at higher ICP power (>700 W) could be explained by a combined effect of lower ion energy, redeposition of etch products, and sputter desorption of adspecies out of the surface prior to etch reaction [Hahn et al., 1999; Hays et al., 1999].

The effect of plasma chemistries on the crystal structure of the etched SBT surface was examined by using XRD patterns of control and etched samples (Fig. 6). The as-grown sample showed polycrystalline structure, displaying peaks of (115), (200), (220), (0010), (0012), and (2010). Although not illustrated, the SBT film etched in $Cl_2/O_2/Ar$ plasma showed quite similar patterns to those of the control sample. However, other chemistries showed different crystalline structures and no peaks of (200). It is also interesting to see

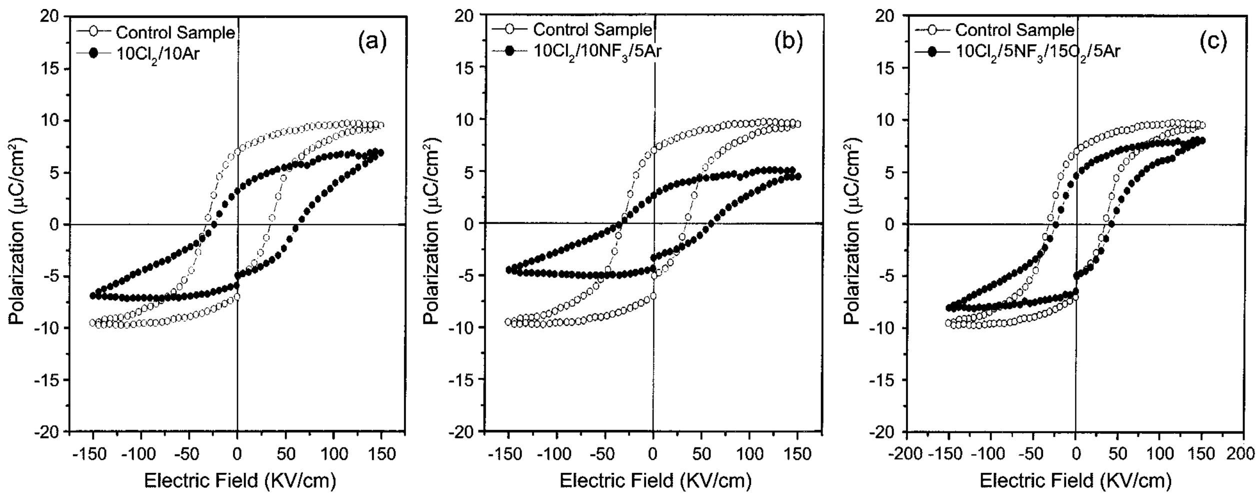


**Fig. 7. P-E hysteresis loops of SBT films etched in different plasma chemistries at 700 W ICP, 150 W rf, and 5 mTorr.**
(a) $Cl_2/Ar$, (b) $Cl_2/NF_3/Ar$, and (c) $Cl_2/NF_3/O_2/Ar$

that $Cl_2/NF_3/O_2/Ar$ showed new peaks of (110), (111), and (008); while $Cl_2/Ar$ and $Cl_2/NF_3/Ar$ plasmas showed a strong peak of (115).

Fig. 7 shows the P-E hysteresis loops of control and etched SBT films. It is seen that the as-grown or control sample exhibits typical ferroelectric hysteresis loop (remnant polarization $(2P_r)$=18.1 μC/cm$^2$, coercive field $(E_c)$=33.5 V/cm). The SBT films etched in $Cl_2/Ar$ and $Cl_2/NF_3/Ar$ plasmas showed substantial degradation of electrical property, which may be attributed to the structure change after the ICP etching. However, $Cl_2/NF_3/O_2/Ar$ showed the least degradation of P-E hysteresis loop compared to other chemistries, resulted in $2P_r$=12.3 μC/cm$^2$, $E_c$=41.9 V/cm. This result indicates that addition of $O_2$ compensates oxygen deficiency, better maintaining the perovskite structure, and thus less plasma damage to the structural and electrical properties of the SBT film. All chemistries also showed a positive shift of the P-E hysteresis loops, compared to that of the control sample. This voltage shift might be attributed to defects such as trapped charges at the interface between the ferroelectrics and electrodes, an oxygen vacancy related defect dipole at the interface, and polar defects [Lee et al., 1999].

## SUMMARY AND CONCLUSIONS

Inductively coupled plasma (ICP) chemistries of $Cl_2/Ar$, $Cl_2/O_2/Ar$, $NF_3/Cl_2/Ar$, and $NF_3/O_2/Cl_2/Ar$ were examined to study the etch characteristics of $SrBi_2Ta_2O_9$ (SBT) thin films. Etch rate was dependent of plasma chemistries and parameters such as ICP source power and rf chuck power. The ICP etching of the SBT film is dominated by physical sputtering at lower pressures mainly due to less recombination of ions and longer mean free path of ions. Addition of $O_2$ played an important role in compensating oxygen depletion as well as stabilizing the SBT structure, and thus suppressed the etch rate. However, $NF_3$ enhanced the etch rate substantially mainly due to reactive fluorine radicals. Maximum etch rates obtained were: 740 Å/min with $Cl_2/Ar$, 320 Å/min with $Cl_2/O_2/Ar$, 1,500 Å/min with $Cl_2/NF_3/Ar$, and 1,600 Å/min with $Cl_2/NF_3/O_2/Ar$ at 5 mTorr, 700 W ICP power and 150 W rf chuck power. The SBT films etched with $Cl_2/NF_3/O_2/Ar$ showed new peaks of (110), (111), and (008), while $Cl_2/Ar$ and $Cl_2/NF_3/Ar$ plasmas showed a strong peak of (115). Electrical properties of the SBT films were quite dependent on plasma chemistries employed. The SBT films etched in $Cl_2/NF_3/O_2/Ar$ plasma showed the least degradation of electrical property in terms of P-E hysteresis loop, having remnant polarization $(2P_r)$=12.3 μC/cm$^2$ and coercive field $(E_c)$=41.9 V/cm and indicating the least plasma damage.

## ACKNOWLEDGMENT

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