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Inductively Coupled Plasma Etching of $Pb(Zr_xTi_{1-x})O_3$ Thin Films in $Cl_2/C_2F_6/Ar$ and HBr/Ar Plasmas

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Abstract−$Pb(Zr_xTi_{1-x})O_3$ thin films were etched in an inductively coupled plasma by using various etch gases such as Cl_2/Ar, C_2F_6/Ar, $Cl_2/C_2F_6/Ar$ and HBr/Ar. The etch rates and etch profiles for each etch gas were investigated. Fast etch rates were obtained in chlorine-containing etch gases (e.g., Cl_2/Ar and $Cl_2/C_2F_6/Ar$), and clean and steep etch profiles were achieved in $Cl_2/C_2F_6/Ar$ or HBr/Ar gases. The gas mixture of Cl_2 and C_2F_6 was proposed to give a fast etch rate and a steep sidewall angle of etched patterns. The optimum gas mixture of $Cl_2/C_2F_6/Ar$ was found by varying the gas ratio of Cl_2 to C_2F_6. On the other hand, HBr/Ar gas as an alternative for etching of the $Pb(Zr_xTi_{1-x})O_3$ films was examined. $Cl_2/C_2F_6/Ar$ and HBr/Ar etch gases were compared with respect to etch rate, etch profile and electrical properties.

Key words: Inductively Coupled Plasma, High Density Plasma Etching, $Pb(Zr_xTi_{1-x})O_3$ Thin Film, $Cl_2/C_2F_6/Ar$, HBr/Ar

INTRODUCTION

Many studies of PZT and PLZT (La-doped PZT) ferroelectric films as a dielectric material for storage capacitors of highly integrated memory devices (e.g., DRAM and FeRAM) have been conducted since these films have high dielectric constant and high remanent polarization [Jeon and Yoo, 1998]. The process development for etching of the PZT thin films is prerequisite for the integration of these memory devices. Various etching processes including ion beam etching (IBE), reactive ion beam etching (RIBE) and reactive ion etching (RIE) have been employed to define the patterns on ferroelectric materials [Vijay et al., 1993; Bale and Palmer, 1999]. In order to overcome the poor selectivity to photoresist mask in a conventional RIE, high density plasma systems such as electron cyclotron resonance (ECR) [Charlet and Davies, 1993] and inductively coupled plasma (ICP) [Chung et al., 1995] were applied. Recently, inductively coupled plasma etching using Cl_2/CF_4 gas was reported [Jung and Lee, 2001]. As the critical dimension of the devices shrinks, a high degree of anisotropic etching is required. The etch studies of PZT films by using a hard mask are under development for this purpose.

In this study, C_2F_6/Ar, Cl_2/Ar and $Cl_2/C_2F_6/Ar$ were investigated and HBr/Ar as an alternative was explored by using a photoresist mask for the anisotropic etching of PZT thin films. The etch damage to the etched ferroelectric capacitors as well as the etch rate and etch profile becomes a key factor in developing the etch process. One of the crucial damages to ferroelectric capacitors was found to be the degradation by hydrogen. For this purpose, the electrical properties of etched ferroelectric capacitors were examined.

EXPERIMENTAL

$Pb(Zr_xTi_{1-x})O_3$ thin films of 2,000 Å in thickness were deposited on Pt coated $Ti/SiO_2/Si$ substrates by a chemical solution deposition process. The deposited PZT films were examined by an x-ray diffractometer (XRD) for the analysis of crystal structure and by field emission scanning electron microscopy (FESEM) for surface morphology, grain shape and grain size. The deposited PZT films were spin-coated with conventional positive photoresist with a thickness of 1.2 µm and patterned by photolithography for etching. The etch equipment used in this study was a high-density inductively coupled plasma reactive ion etch system (ICPRIE) which has a load-lock chamber and a He backside cooling system to wafer platen [Chung, 1998]. The coil, which was connected to 13.56 MHz RF power supply, was wound around the ceramic chamber to generate a high-density plasma. An RF bias voltage induced by RF power at 13.56 MHz was capacitively coupled to the substrate susceptor to control ion energy.

The etch rates were measured by a surface profiler and the etch profiles were observed by the FESEM. By using Cl_2/Ar, C_2F_6/Ar, $Cl_2/C_2F_6/Ar$ and HBr/Ar discharges, the dry etching of PZT films was studied varying the concentration of etch gas at fixed etching conditions which included coil RF power, dc-bias voltage to substrate and gas pressure. The $Cl_2/C_2F_6/Ar$ etch gas was optimized to give a fast etch rate and a clean and steep etch profile. As an alternative etch gas, HBr/Ar was tried despite the possibility of hydrogen damage to the ferroelectric capacitor. After etching of PZT films, platinum (Pt) thin films were deposited as an upper electrode for the electrical properties of Pt/PZT/Pt capacitors.

RESULTS AND DISCUSSION

The etch rates of PZT films with C_2F_6/Ar and Cl_2/Ar gases are shown in Fig. 1. The etching condition used in this experiment was coil power of 600 W, gas pressure of 5 mTorr, and 300 V dc-bias to the wafer susceptor. This condition was fixed as a standard etch condition through the entire experiments. As the concentration of each gas increases, the etch rates increase but decrease with further increasing concentration. It indicates that the etching of PZT films with these gases basically exhibits a characteristic of reactive ion etching mechanism. The reason for decreasing etch rate with fur-

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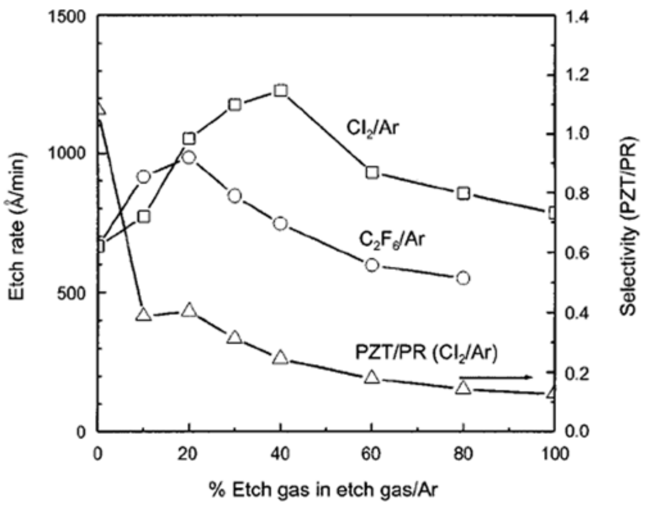

Fig. 1. Etch rates of PZT films as a function of gas concentration.

ther increasing of the gas concentration is explained by the fact that the excess etch gas inhibits the sputtering of ions to the film surface by forming a thin layer composed of Cl or F components, resulting in a slow etch rate [Hahn and Pearton, 2000]. It is observed that the maximum etch rate with C_2F_6/Ar gas reaches earlier than that with Cl_2/Ar. It means that the formation of inhibiting layer in C_2F_6/Ar takes place more easily and faster than in Cl_2/Ar. However, the etch rates were faster in Cl_2/Ar than in C_2F_6/Ar.

Fig. 2 shows the SEM photographs of the PZT films etched by C_2F_6/Ar and Cl_2/Ar gases. In the case of C_2F_6/Ar, thick polymer-like films along the pattern were observed at 40 and 60% C_2F_6. This is because the fluorine in C_2F_6 gas forms the etch products of metal fluorides with PZT films, but the volatility of these etch products is relatively low, resulting in thick etch residues. It implies that these polymer layers may be utilized as a passivation for an anisotropic etching. On the other hand, the etch patterns by Cl_2/Ar gas displayed clean etch profile, but the selectivity to photoresist mask was poor. One can see the etched edge regions of the pattern due to the lateral erosion of photoresist mask [Fig. 2(c)]. As the Cl concentration increases, this phenomenon becomes severer. It indicates that any sort of passivation layer along the sidewall is necessary for the Cl_2/Ar chemistry.

Therefore, the use of a gas mixture of Cl_2 and C_2F_6 was attempted for utilizing the respective advantages of Cl_2 and C_2F_6 gases. To obtain an optimum gas ratio of Cl_2 to C_2F_6, the etch rates of PZT films were examined varying the gas ratio from 1/1 to 9/1 at constant 30% $(Cl_2+C_2F_6)$/70%Ar. As can be seen in Fig. 3, as the chlorine concentration increases, the enhancements of the etch rate are observed. The corresponding SEM photographs at various gas ratios are given in Fig. 4. The etch residues along the etched patterns took place at the gas ratios of Cl_2/C_2F_6=1/1, 3/1 and 6/1 [Figs. 4(a)-4(c)], whereas a clean etch profile was obtained at the gas ratio of Cl_2/C_2F_6=9/1 [Fig. 4(d)]. As a next step, the overall gas concentration at the fixed

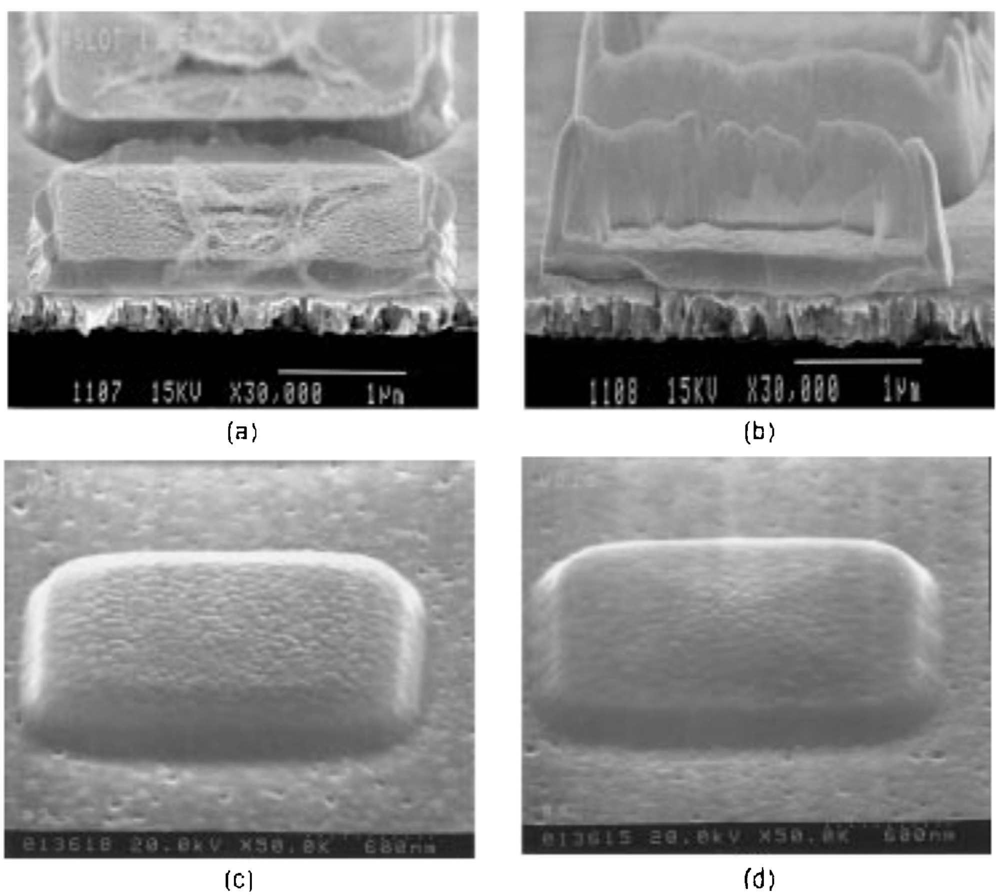

Fig. 2. Etch profiles of PZT films etched in (a) 40% C_2F_6/Ar gas, (b) 60% C_2F_6/Ar gas, (c) 40% Cl_2/Ar gas, (d) 60% Cl_2/Ar gas.

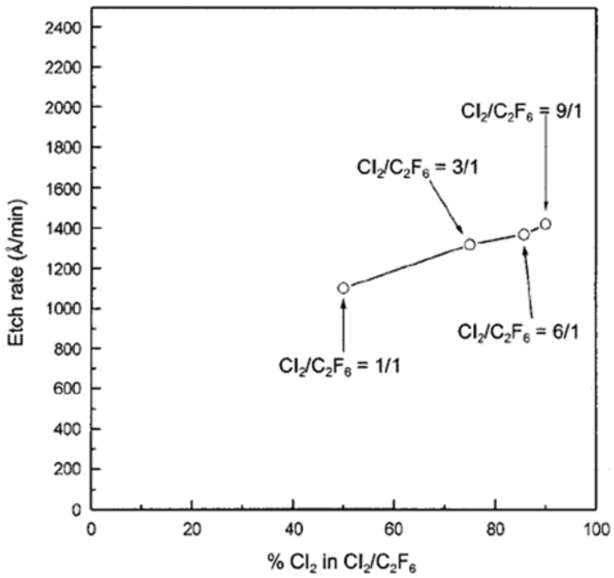

Fig. 3. Effect of gas ratio of Cl_2/C_2F_6 on etch rate.

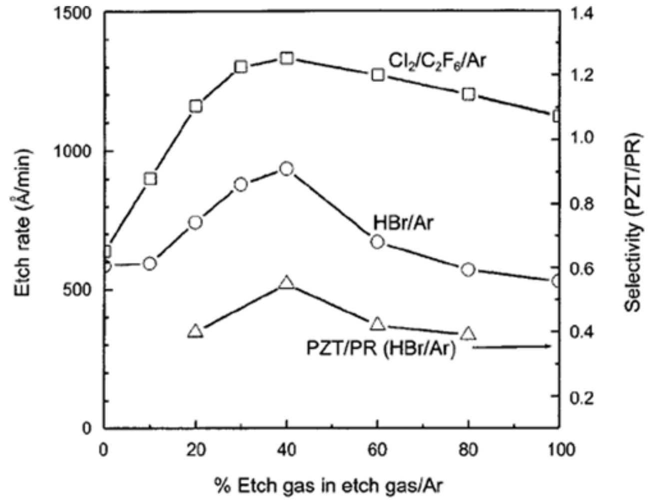

Fig. 5. Etch rates of PZT films as a function of gas concentration.

gas ratio of Cl_2/C_2F_6=9/1 was changed to see the effect of gas concentration on the etch rate (Fig. 5). With increasing the gas concentration the etch rate shows a maximum point and then starts to decrease by similar manner to Cl_2/Ar and C_2F_6/Ar gases. The overall etch rate was somewhat faster in Cl_2/C_2F_6/Ar than in Cl_2/Ar and C_2F_6/Ar. Fig. 6 shows the SEM photographs of PZT films etched at the gas concentrations of 10, 30 and 60% ($Cl_2+C_2F_6$)/Ar. The etch profile for 10% ($Cl_2+C_2F_6$) was steep but had a little etch residue along the etched sidewall. At 30 and 60% ($Cl_2+C_2F_6$) gas concentrations, clean etch profiles were achieved without any residues. How-

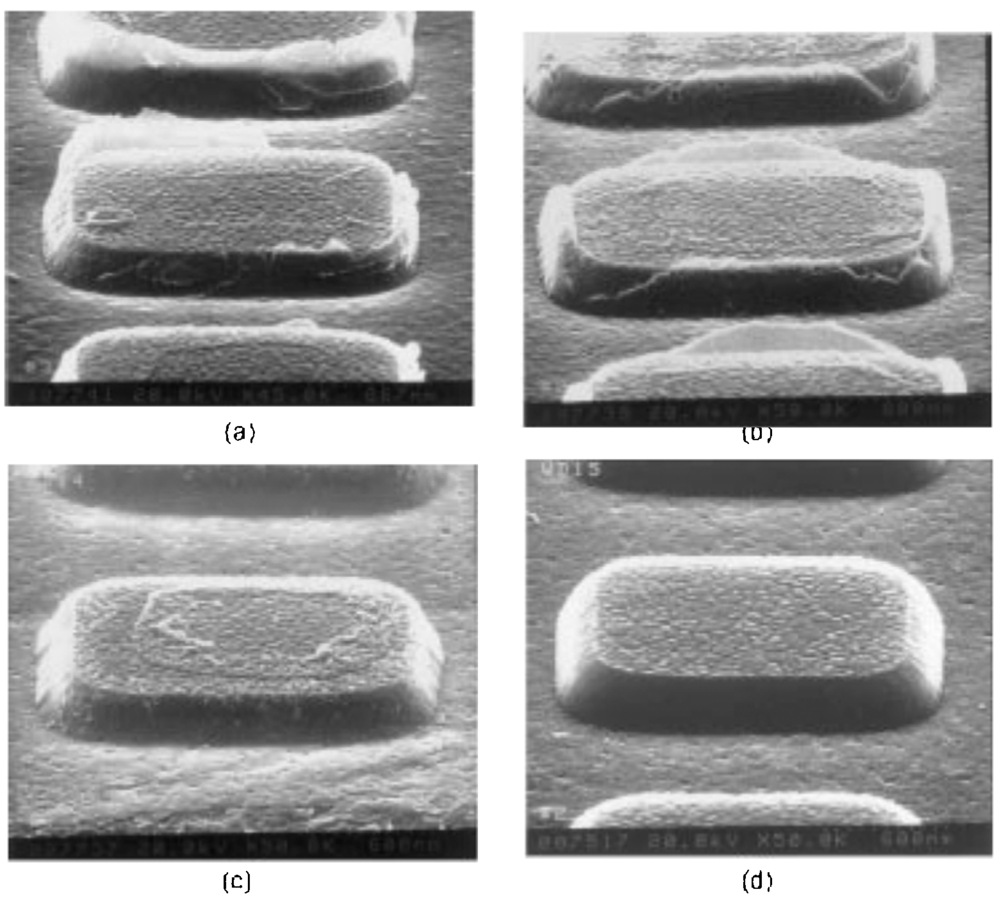

Fig. 4. Effect of gas ratio of Cl_2/C_2F_6 on etch profile.
(a) Cl_2/C_2F_6=1/1, (b) Cl_2/C_2F_6=3/1, (c) Cl_2/C_2F_6=6/1, (d) Cl_2/C_2F_6=9/1

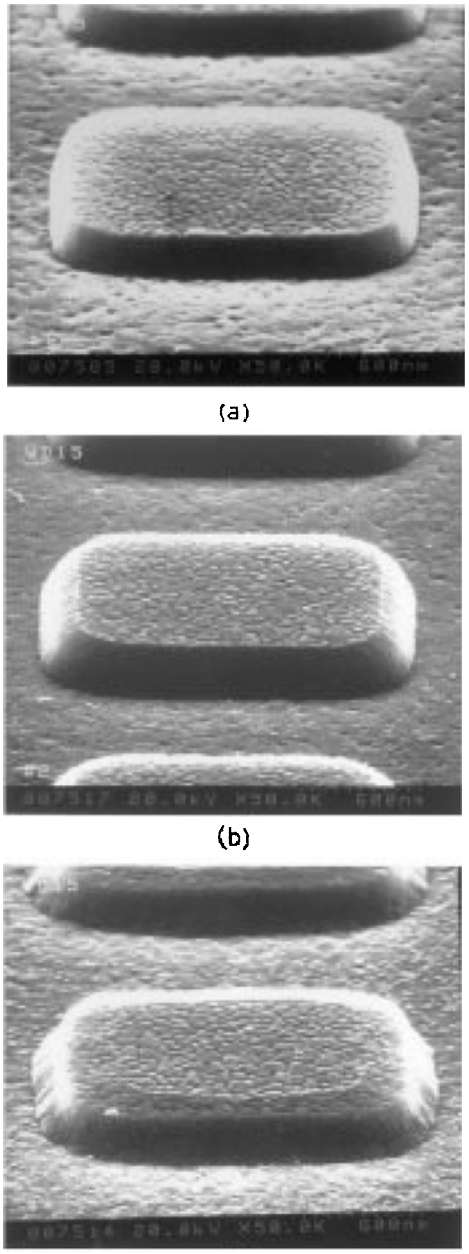

Fig. 6. Effect of gas concentration of $Cl_2/C_2F_6/Ar$ on etch profile.
(a) 10%(Cl_2+C_2F_6), (b) 30%(Cl_2+C_2F_6), (c) 60%(Cl_2+ C_2F_6)

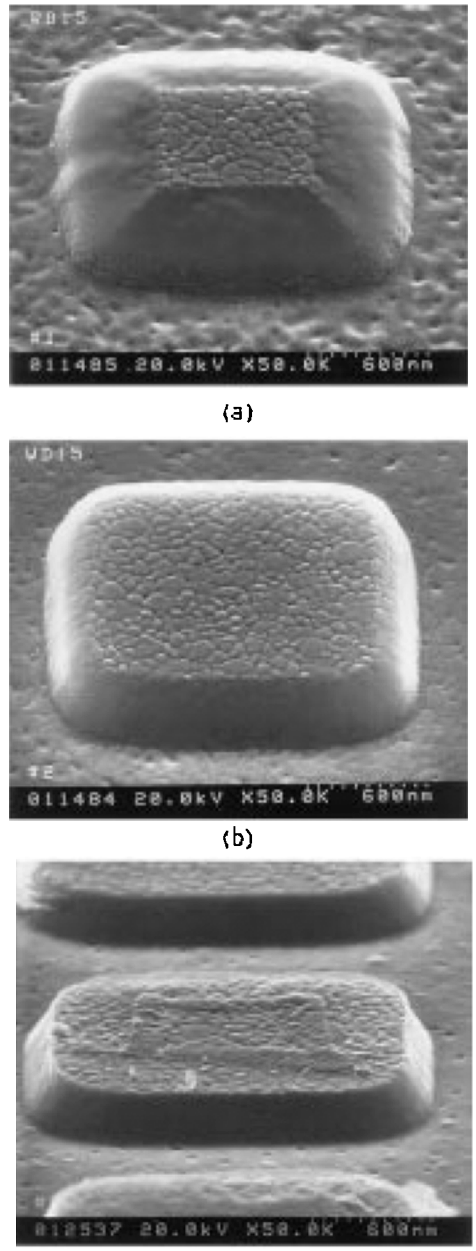

Fig. 7. Effect of gas concentration of HBr/Ar on etch profile.
(a) 10% HBr, (b) 30% HBr, (c) 60% HBr

ever, as the gas concentration increased, the slope of etched sidewall became shallow because of the increased chlorine content. As a result, a high degree of anisotropic profile could be achieved at 30% (Cl_2+C_2F_6)/Ar.

HBr/Ar gas was also investigated as an alternative gas, as shown in Fig. 5. It was expected that HBr gas could make volatile etch products and give high selectivity to photoresist mask. The change of etch rate as a function of gas concentration (HBr/Ar) showed the same trend as the $Cl_2/C_2F_6/Ar$ gas mixture. The etch rate with $Cl_2/C_2F_6/Ar$ was faster than that with HBr/Ar. The etch profiles by HBr/Ar gas are shown in Fig. 7. The profile at 10% HBr/Ar shows a laterally eroded etch profile, which is attributed to the corrosive nature of Br. As the addition of HBr gas increased, the slope of etched sidewall became steeper with the help of passivation layer by hydrogen in HBr. Finally, the electrical properties of ferroelectric capacitors etched with $Cl_2/C_2F_6/Ar$ and HBr/Ar gases are compared in Fig. 8. The etch conditions used here were optimized for each etch gas, respectively. Hysteresis loop and Q to V curve were almost identical for both gases. An I-V curve also exhibited a similar trend, but the breakdown in the case of HBr/Ar seemed to happen at somewhat lower voltage than in $Cl_2/C_2F_6/Ar$.

CONCLUSIONS

Reactive ion etching of PZT thin films masked with a photoresist was performed in high density inductively coupled plasma. The

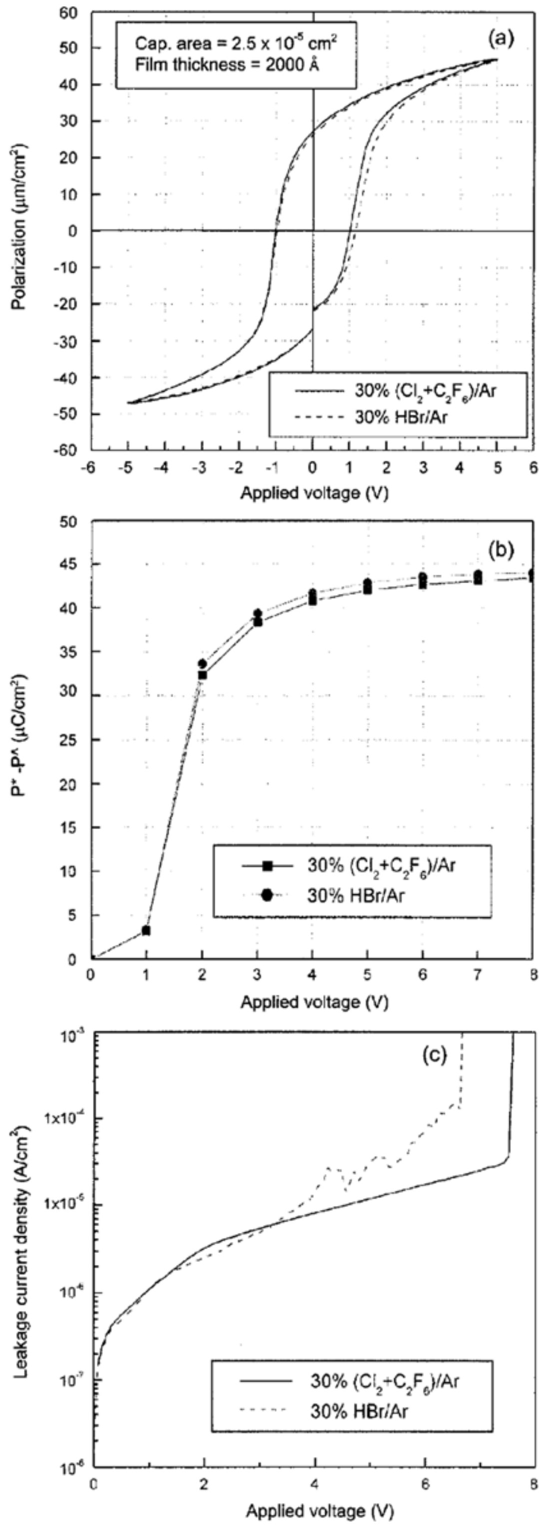

Fig. 8. Electrical properties of ferroelectric capacitors etched by $Cl_2/C_2F_6/Ar$ and HBr/Ar gases.
(a) hysteresis loop, (b) Q to V curve, (c) I-V curve

Cl_2/Ar, C_2F_6/Ar, $Cl_2/C_2F_6/Ar$ and HBr/Ar gases were examined for fast etch rate and high degree of anisotropic etching without etch residues. The Cl_2/Ar gas for etching of the PZT films gave rise to faster etching than C_2F_6/Ar and HBr/Ar gases. The clean and steep etch profiles were obtained in Cl_2/Ar and HBr/Ar chemistries. By employing $Cl_2/C_2F_6/Ar$ among the various etch gases, the etching process for PZT thin films was developed to obtain a high etch rate (1,000-1,500 Å/min) and a clean etch profile without redeposits and residues. The sidewall angle of etched PZT films was in the range of 50-80°. Under the optimum etch condition, the etch rate of 1,300 Å/min and the etched sidewall angle of 80° were achieved with a photoresist mask. The electrical properties (hysteresis loop, Q to V, I-V curves) of PZT capacitors etched by $Cl_2/C_2F_6/Ar$ and HBr/Ar gases showed similar behaviors and the etch gas combination seemed to have little effect on electrical properties. These etch chemistries were proposed as a basis for the etching of PZT films using a hard mask.

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