The Electrical Improvement of PZT Thin Films Etched into CF$_4$/(Cl$_2$+Ar) Plasma

Seong-Mo Koo, Kyoung-Tae Kim, and Chang-Il Kim[a]
School of Electrical and Electronic Engineering, Chung-ang University,
221 Heuksuk-dong, Dongjak-gu, Seoul 156-756, Korea

[a]E-mail : cikim@cau.ac.kr

(Received September 30 2004, Accepted December 7 2004)

The PZT thin films are one of well-known materials that has been widely studied for ferroelectric random access memory (FRAM). We etched the PZT thin films by CF$_4$/(Cl$_2$+Ar) plasma and investigated improvement in etching damage by O$_2$ annealing. The maximum etch rate of the PZT thin films was 157 nm/min and that the selectivity of the PZT thin films to Pt was 3.1 when CF$_4$ (30 %) was added to a Cl$_2$ (80 %)/Ar (20 %) gas mixing ratio. To improve the ferroelectric properties of PZT thin films after etching, the samples were annealed for 10 min at various temperatures in O$_2$ atmosphere. After O$_2$ annealing, the remanent polarization of the as-deposited films was 34.6 $\mu C/cm^2$ and the sample annealed at 650, 550, and 450 °C was 32.8, 22.3, and 18.6 $\mu C/cm^2$, respectively. PZT thin films with O$_2$ annealing at 450 °C retained 77 % of their original polarization at 106 cycles. Also as the annealing temperature increased, the fatigue properties improved. And the leakage current was decreased gradually and almost recovered to the as-deposited value after the annealing at 650 °C.

Keywords : Etching, PZT, Ferroelectric properties

1. INTRODUCTION

Lead zirconate titanate [Pb (Zr$_x$Ti$_{1-x}$)O$_3$, PZT] is well-known material that has been widely studied for ferroelectric random access memory (FRAM) due to the desirable properties such as high permittivity, high remnant polarization, fast switching speed, high Curie point and resistivity in thin film form[1-3]. Therefore, FRAMs can combine the high performance and longevity of dynamic random access memories (DRAMs) and static random access memories (SRAMs) with the non-volatility, and ability to store data without power, of read only memory. Because of their excellent potential, FRAMs are in grate demand for use in various fields such as in electronic cards and tags portable software media smart sensors and silicon disks. Many fabrication methods such as sol-gel, chemical vapor deposition (CVD), magnetron sputtering and pulsed laser deposition have been used to prepare PZT thin films[4-7]. Among then the sol-gel technique offers a simple and low-cost process to prepare high quality thin films. Also, etching processes for PZT films have been developed as well as deposition processes. Many studies have been reported on the etching of PZT films using reactive ion etching (RIE), magnetically enhanced reactive ion etching (MERIE) and high-density plasma etching, such as electron cyclotron resonance (ECR) and inductively coupled plasma (ICP). Among these techniques, the ICP provides lower ion energy and the capability to operate at lower chamber pressure. Moreover, ion fluxes and ion energy can be controlled separately, thus increasing flexibility in optimizing etch responses. However, the plasma etch process degrades the electrical properties because of physical damage and chemical residue contamination. The physical damage due to the displacement of atoms is believed that it was caused by the bombardment of the energetic charged particles in the plasma. The physical damage alters the near-surface region of the ferroelectric material, exposed to the plasma and thus changes its electrical properties. Also PZT thin films have same problems of etching. Nevertheless, the problem of etching-induced damage remains important, and post-etching treatment is required to recover the structure and ferroelectric properties[8].

In this paper, we investigated the etch rate and selectivity of PZT thin films for device fabrication and observed the recovery etching damage in PZT thin films by annealing. PZT thin films were etched with CF$_4$/

(Cl_2+Ar) gas chemistries in inductively coupled plasma (ICP) etching system. We annealed them using a conventional furnace for 10 min at various temperatures in an O_2 atmosphere after etching. Then, the polarization–electric field (P-E), leakage current, and fatigue are compared to examine the etching damage and the recovery of etching damage after the O_2 annealing.

2. EXPERIMENTAL

The PZT thin films of 300 nm thickness were prepared on Pt/Ti/SiO_2/Si substrates by sol-gel process. The sol-gel solution for PZT thin films was prepared from lead acetate-trihydrate, zirconium n-propoxide and titanium isopropoxide. Acetic acid and 2-methoxyethanol were used as solvents. The PZT solution had a molar ratio of Pb/(Zr+Ti) = 1.1 and Zr/Ti = 30/70. The PZT (30/70) precursor solution was spin-coated on a Pt/Ti/SiO_2/Si (100) substrate by using a spinner operated at 3500 rpm for 30 sec, and followed by pyrolysis at 350 °C for 10 min to remove organic materials. The spin coating and drying was repeated to obtain PZT thin films with a thickness of 300 nm. Amorphous films were sintered at 650 °C for 1 hr to crystallize them into a perovskite structure in a preheated furnace. To investigate the ferroelectric properties of etched PZT thin films, a Pt electrode of 150 nm in thickness and a diameter of 240 μm was formed on the PZT films using rf sputtering. Pt electrode was used as shadow dot mask in etch process and a top electrode in electrical test. The PZT films were etched by an inductively coupled plasma (ICP) system. The chamber was evacuated to a base pressure below 0.133 mPa and then the etching gas was introduced to the chamber through a mass flow controller. A 13.56 MHz rf power generator was connected to planar spiral Cu coil separated by 2.4 cm thick quartz window through a matching network on the top of the process chamber. Another 13.56 MHz rf power generator was applied to the substrate to induce the dc-bias voltage to the wafer.

The PZT thin films were etched at an additive CF_4 in Cl_2 (80 %)/Ar (20 %) in inductively coupled plasma (ICP). Total gas flow rate, chamber pressure, rf power, substrate bias voltage, and substrate temperature were 20 sccm, 2 Pa, 700 W, -200 V, and 30 °C, respectively. The etch rate was measured by the surface profiler (KLA Tencor, α-step 500). In order to understand the etching damage and recovery properties, we annealed the PZT thin films using a conventional furnace for 10 min at various temperatures in an O_2 atmosphere. The polarization-electric field (P-E) curves and fatigues were measured with a precision workstation ferroelectric tester (Radiant Technologies, USA). The leakage current was measured using a parameter analyzer (HP4156C).

3. RESULT AND DISCUSSION

The PZT thin films were etched with CF_4 added into a Cl_2/Ar gas mixture having the ratio of 8/2 at a substrate temperature of 30 °C, an rf power of 700 W, a dc-bias voltage of -200 V and chamber pressure of 2 Pa. In the etching process of PZT films with the Cl_2-based plasma, Ar increases Cl radicals and ions, thus the chemical reactions between Cl radicals and the surface of PZT films increase and non-volatile etching byproducts such as metal chlorides and metal fluorides effectively removes. This indicates that ion-assisted chemical etching is effective for etching PZT thin films. The addition of CF_4 is expected to increase the rate of chloride atom generation, while the presence of Ar accelerates chemical reactions on the PZT surface through the ion-stimulated desorption of reaction products[9,10]. Experimental results are shown in Fig. 1. The maximum etch rate of the PZT thin films was 157 nm/min and that the selectivity of the PZT thin films to Pt was 3.1 when CF_4 (30 %) was added to a Cl_2/Ar gas mixing ratio of 8/2.

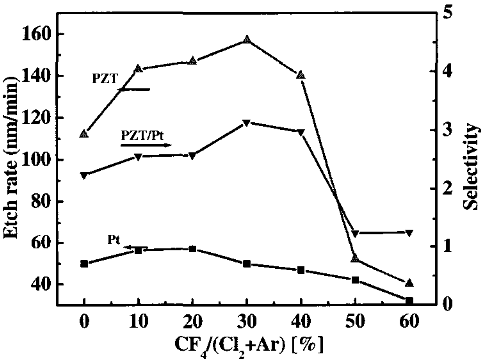

Fig. 1. Etch rate and selectivity of PZT thin films to Pt as an addition of CF_4 in Cl_2 (80 %)/Ar (20 %) plasma.

The etch rate of PZT thin films increases as additive CF_4 increases up to 30 % and decreased with further increase of additive CF_4. The increased etch rate of PZT can be suggested by C-O formation and an increased Cl concentration with addition of a small amount of CF_4 by the following reactions in $CF_4/(Cl_2+Ar)$ plasma. That is, the chemical reactions occurs as follows: $C + M\text{-}O \rightarrow M + CO$, $Cl_2 + F \rightarrow FCl + Cl$, and $Cl_2 + CF_2 \rightarrow ClF_2 + Cl$ [11].

Figure 2 shows the comparison of hysteresis loops for as-deposited, as well as etched PZT films before and after O_2 annealing. The results show that the etching process decreases the remanent polarization (Pr), while after O_2 annealing with various temperature the value of the remanent polarization shows gradual improvement, but remains lower than for the as-deposited film. The remanent polarization of the as-deposited films was 34.6 μC/cm^2 and the sample annealed at 650, 550, and 450 °C was 32.8, 22.3, and 18.6 μC/cm^2, respectively. We suppose that the decrease in the remanent polarization is explained by the physical and chemical damage to the PZT surface. In other words, the ion bombardment has a degrading effect on ferroelectric properties and the destruction of the structure of PZT thin films.

Figure 3 shows the fatigue properties as functions of the number of switching cycles for a ±5 V bipolar square wave at a frequency of 50 kHz under various conditions. PZT thin films with O_2 annealing at 450 °C retained 77 % of their original polarization at 106 cycles.

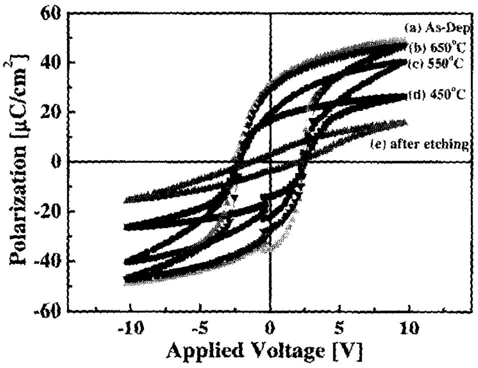

Fig. 2. Hysteresis curves of the annealed PZT thin films after etching: (a) As-deposited PZT thin films; (b) re-annealing at 650 °C; (c) re-annealing at 550 °C; (d) re-annealing at 450 °C; and (e) PZT thin film etched in $CF_4/(Cl_2+Ar)$ plasma.

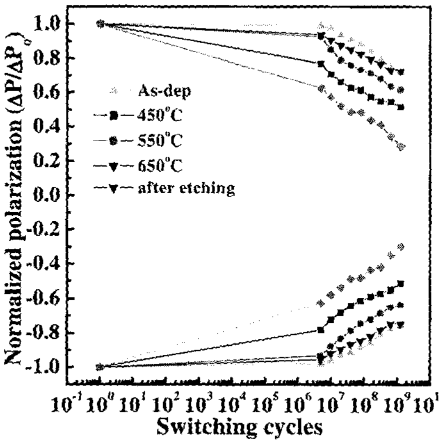

Fig. 3. Fatigue characteristics for PZT thin films at various temperatures in O_2 atmosphere. Polarization after O_2 annealing is caused by the improvement in crystalline structure.

However, as the O_2 annealing temperature increases, the switching polarization was recovered. The remanent polarization was improved to 94 % in O_2 annealing at 650 °C. It means that ferroelecetric behavior consistent with the dielectric nature of Ti_xO_y is recovered by O_2 recombination during re-annealing process[12]. And because the decrease in fatigue properties may be attributed to an increase in the number of oxygen vacancies, annealing provides substitution of vacancies by O atoms. Therefore, after annealing the number of oxygen vacancies decreased and the fatigue properties improved.

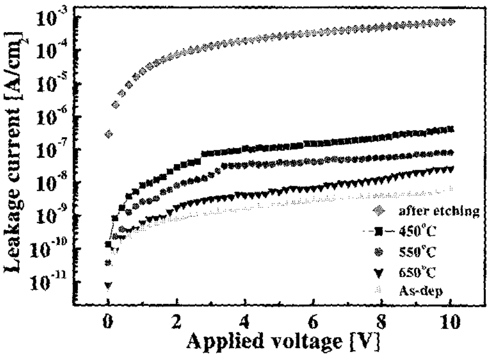

Fig. 4. I-V characteristics of PZT thin films as a function of annealing temperatures.

Figure 4 compares the current-voltage (I-V) characteristics of the as-deposited to the annealed samples with the various temperatures. The leakage current of the PZT sample annealed at 450 °C was seriously increased as similar as that of etched sample. As increasing the annealing temperature, the leakage current was decreased gradually and almost recovered to the as-deposited value after the annealing at 650 °C. These results show that the charges accumulated at the top electrode-ferroelectric interface can modify the interfacial Schottky barrier. These charges will also accumulate on the sidewall of the PZT pattern so that the domains in the PZT films near the interface can be pinned or locked up at discontinuities such as grain boundaries and charged point defects. Therefore, we suppose that the charges pinned or locked up at the top electrode-ferroelectric interface can be released from the sites during the annealing process.

4. CONCLUSION

We investigated the ferroelectric properties of the PZT thin films that was damaged by $CF_4/(Cl_2+Ar)$ plasma, was recovered with O_2 re-annealing. The PZT thin films were etched for 1 min in an ICP system using Cl_2/Ar

plasma with a gas mixing ratio of 8/2 and CF_4 addition. The maximum etch rate of PZT thin films was 157 nm/min at 30 % additive CF_4 into Cl_2 (80 %)/Ar (20 %). After etched, the ferroelectric properties (the remanant polarization, fatigue resistance, leakage current) in the PZT sample etched in the CF_4/(Cl_2+Ar) plasma was seriously degraded. In order to improve the ferroelectrical properties, the etched PZT thin films were annealed for 10 min at various temperatures in an O_2 atmosphere. Then the attenuation of the ferroelectric properties by plasma-induced damage was recovered to as-deposited conditions. These results show that the ferroelecetric behavior consistent with the dielectric nature of Ti_xO_y is recovered by O recombination during the re-annealing process. And the accumulated charges at the top electrode-ferroelectric interface can modify the interfacial schottky barrier during the etching process. These charges will also accumulate on the sidewall of the PZT pattern so that the domains in the PZT films near the interface can be pinned or locked up at discontinuities such as grain boundaries and charged point defects. However, the charges pinned or locked up at the top electrode-ferroelectric interface can be released from the sites and chemical residue may be effectively removed during the annealing process in oxygen ambient.

REFERENCES

[1] K. Uchino, "Piezoelectric Actuators and Ultrasonic Motors", Kluwer Academic Publisher, Boston, 1997.

[2] R. Moazzami, "Ferroelectric thin film technology for semiconductor memory", Semicond. Sci. Technol., Vol. 10, No. 4, p. 375, 1995.

[3] C. A. Paz de Araudjo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, "Fatigue-free ferroelectric capacitors with platinum electrodes", Nature, Vol. 374, No. 6523, p. 627, 1995.

[4] K. D. Budd, S. K. Dey, and D. A. Payne, "Sol-gel processing of $PbTiO_3$, PZT, and PLZT thin film", Br. Ceram. Proc., Vol. 36, p. 107, 1985.

[5] M. Shimuzu, M. Sugiyama, H. Fujisawa, and T. Shiosaki, "Control of orientation of Pb (Zr, Ti)O_3 thin films using $PbTiO_3$ buffer layer", Jpn. J. Appl. Phys., Vol. 33, No. 9B, p. 5167, 1994.

[6] R. Takayama and Y. Tomita, "Preparation of epitaxial Pb (Zr_xTi_{1-x})O3 thin films and their crystallographic, pyroelectric, and ferroelectric properties", J. Appl. Phys., Vol. 65, No. 4, p. 1666, 1989.

[7] Y. Lin, B. R. Zhou, H. B. Peng, B. Xy, H. Chen, F. Wu, H. J. Tao, Z. X. Zhao, and J. S. Chen, "Growth and polarization features of highly (100) oriented Pb ($Zr_{0.53}Ti_{0.47}$)O_3 films on Si with ultrathin SiO_2 buffer layer", Appl. Phys. Lett., Vol. 73, No. 19, p. 2781, 1998.

[8] W. Pan, S. B. Desu, I. K. Yoo, and D. P. Vijai, "Reactive ion etching of Pb (Zr_xTi_{1-x})O_3 and RuO2 films by environmentally safe gases", J. Mater. Res., Vol. 9, No. 11, p. 2976, 1994.

[9] W. Pan, C. L. Thio, and S. B. Desu, "Reactive ion etching damage to the electrical properties of ferroelectric thin films", J. Mater. Res., Vol. 13, No. 2, p. 362, 1998.

[10] S. A. Mansour, G. L. Liedl, and R. W. Vest, "Microstructural developments and dielectric properties of rapid thermally processed PZT thin films derived by metallo-organic decomposition", J. Am. Ceram. Soc., Vol. 78, p. 1617, 1991.

[11] J. K. Jung and W. J. Lee, "Dry etching characteristics of Pb (Zr,Ti)O_3 films CF_4 and Cl_2/CF_4 inductively coupled plasmas", Jpn. J. Appl. Phys., Vol. 40, No. 1, p. 1415, 2001.

[12] N. A. Basit and Hong Koo Kim, "Crystallization of Pb (Zr,Ti)O_3 films prepared by radio frequency magnetron sputtering with a stoichiometric oxide target", J. Vac. Sci. Technol., Vol. A 13, No. 4, p. 2214, 1995.