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Reactive Ion Beam Etching of PZT Thin Films

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Lead titano-zirconate ferroelectric thin films have developed a great interest for their applications in memory devices, and more recently in microelectromechanical systems because of their interesting piezoelectric properties. The patterning has become an essential element for PZT integration in devices. Reactive ion beam etching of sputtered PZT(54/46) thin films has been performed using Ar/CHF_3 gas. The dependence of etch rate and selectivity with the etching parameters has been investigated. PZT etch rate and selectivity reaches 900 Å/min and 7.5 respectively. We have evaluated the PZT surface damage by contact mode AFM. It appears that the roughness increases after ion bombardment. We have observed electrical damaged. These degradations are underlined by carrying out C(V) and hysteresis loops before and after etching.

Keywords: PZT; reactive ion beam etching; Ar/CHF_3; etching damage

I. INTRODUCTION

Ferroelectric thin films have developed a great interest for their applications in microelectromechanical systems (MEMs). $Pb(Zr_{0.54},Ti_{0.46})O_3$ (PZT) thin films is one of the most used material because of their interesting piezoelectric properties. Patterning of PZT films has become an essential element of device fabrication. Several techniques have been developed for etching: wet chemical etching [1], ion beam etching (IBE) [2], reactive ion etching (RIE) [3–5], electron cyclotron resonance (ECR) etching [6], and inductively coupled plasma (ICP) etching [7].

The RIE is widely used because it provides, in some etching conditions, high etch rate, high degree of anisotropy and selectivity. Various gas mixtures have been investigated: Cl_2/C_2F_6/Ar [7], Cl_2/Ar [6], CF_4/CCl_4/Ar [8], Cl_2/BCl_3 [9]. Influence of etching parameters on the electrical damage evolution has already been studied in the case of chemically assisted bombardment. It seems that both effects including the physical damages and the presence of chemical residual species on the film surface are not clearly separately

studied. However, it is currently assumed that particles bombardment is primarily responsible for the etching whatever the process [10, 11].

In this article, a study has been carried out for achieving practical etch for the PZT films by using an ion beam etcher. We examined gas such as pure Ar and a mixture of Ar/CHF_3. The influence of gases chemistries and etch parameters were analyzed in terms of the etch rate, the surface morphology, and the dielectric and polarization-electric field (P-E) loops.

II. EXPERIMENTAL PROCEDURE

$Pb(Zr_{0.54},Ti_{0.46})O_3$ thin films were deposited on Pt/Ti/SiO_2/Si substrates by rf magnetron sputtering with a thickness in the range of 0.9 μm to 1.2 μm. The sputtering conditions are given elsewhere [12]. The PZT films were annealed at 625°C for 30 min to form the PZT perovskite phase.

Ion beam etching (IBE) of PZT was investigated by using Veeco Microetch 3″. This system, described elsewhere, was equipped with a Kaufman type source [13].

The several films were coated with conventional photoresist (PR) Microposit S1813 from Shipley that was patterned by exposure in a mask aligner. The surface microstructure of unetched and etched PZT was characterized by Atomic Force Microscopy (AFM). Imaging in the contact mode AFM was carried out using a Park Scientific Instruments Autoprobe CP.

Pt top electrodes were sputtered through a shadow mask on etched PZT. We have evaluated the electrical properties after etching, and we have compared the results with those obtained for unetched samples on the aim to determine the extent of IBE effect. Capacity, tanδ, and C(V) were performed using an impedance analyser HP4192A at a frequency of 10 kHz and an alternative voltage $V_{ac} = 100$ mV. The ferroelectric loops P(E) were measured using a standardized Radiant RT6000 system. Measurements were made after a top electrode annealing at 500°C. For a greatest clearness in the presentations of our results, we have given them in percentage of decrease (−) or percentage of increase (+) as compared to the unetched PZT.

III. RESULTS AND DISCUSSION

a) Etch Rate and Selectivity

The etch rate of PZT, and the feasibility of using PR, Pt and Ti as etch mask, were first examined as a function of the CHF_3 concentration in Ar/CHF_3

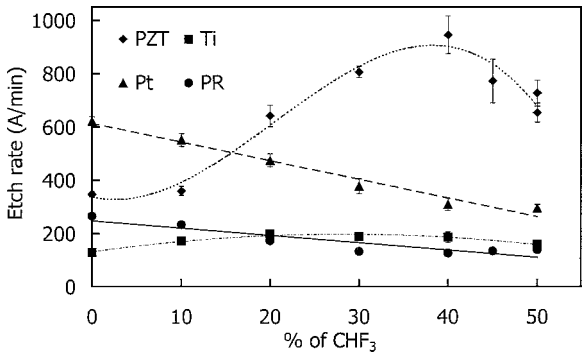


Figure 1. Effect of the concentration of a reactive gas on the etch rate of PZT, PR, Ti and Pt (acceleration voltage = 800 V, current density = 0.7 mA/cm^2).

discharges (Fig. 1). Samples were etched with a varying Ar/CHF_3 gas-mixing ratio at a pressure of 0.2 mT, an acceleration voltage of 800 V and a current density of 0.7 mA/cm^2. The PZT etch rate increases considerably with the increase of the CHF_3 content, as long as the percentage of CHF_3 does not exceed 40. The maximum etch rate of the PZT thin film is around 95 nm/min in comparison with an etch rate of 38 nm/min obtained with pure physical beam etching. This implies that a strong chemical etching effect is involved. The CHF_3 gas catalyzes some chemical reaction when it is present in around 30–40%. This means that PZT thin films can be removed more easily with reactive etching rather than with only physical sputtering of Ar ion bombardment. Above 40% of CHF_3 contained in the etching gas, the effectiveness of the chemical and physical etching combination is less. At higher CHF_3 contents the decrease of the etching rate can be attributed to the lower concentration of energetic Ar ions. This can affect the breaking of the bond at the PZT surface as well as the sputter desorption efficiency of etch products from the surface. Below 60% argon, physical etching is also insufficient to allow an optimal interaction of radicals like F with PZT surface.

Therefore, the PR and platinum etch rate decreases considerably with increasing the content of CHF_3. This indicates that no reactive etching can occur for PR and platinum with CHF_3.

Figure 2 illustrates the selectivity evolution with varying Ar/CHF_3 gas mixing ratio. The selectivities are defined as the ratios between PZT etch rate and Pt, Ti or photoresist etch rate. A large selectivity of PR to PZT was obtained. Indeed, on one hand, the CHF_3 is responsible for the etch rate of PR decreasing, and on the other hand, the PZT etch rate is improved by

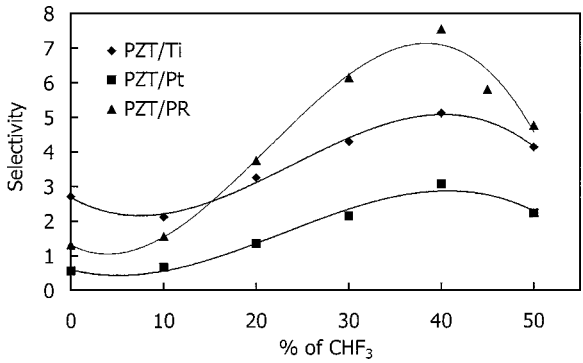


Figure 2. Influence of the CHF_3 content in the etching gas mixture on the selectivity of PZT to PR, Ti and Pt (acceleration voltage = 800 V, current density = 0.7 mA/cm^2).

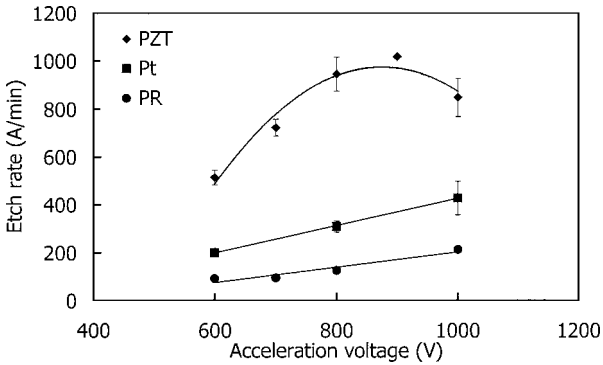
CHF_3 adding. The selectivity of PR to PZT is high and exceeds the value of 7. With a selectivity of Ti to PZT around 5, Ti can be used as metallic mask to etch PZT films.

Figures 3a and 3b illustrate etch rate evolution as a function of the acceleration voltage (the current density is fixed to 0.7 mA/cm^2) and as a function of the current density (the acceleration voltage is fixed to 800 V) respectively. The gas mixture is 60%Ar/40%CHF_3.

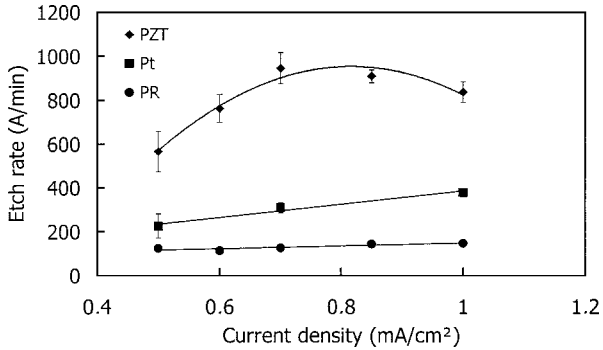
We observe in both cases (Figs. 3a and 3b) an increase of the speed of etching when the parameter considered increases. The behavior is the same for the PZT but above a voltage acceleration higher than 800 V and a current density higher than 0.8 mA/cm^2 the etch rate decreased. In reference [13] we have shown that with a pure argon beam the best selectivity ratio with IBE is obtained with a current density as low as possible for a given acceleration voltage. That is not any more the case for reactive etch: indeed for high acceleration voltage and current density, the selectivities decrease because of the PZT etch rate decrease. This effect may result in an effectiveness of the physical effect of etching not leaving enough time to the chemical effect to act, the result being then overall less good.

b) Surface Morphology

The roughness, for different etching conditions, is characterized by the r_{ms} (r_{ms} is defined as the root mean square). For example, etched PZT films at 800 V, 0.7 mA/cm^2 with gas mixture 60%Ar/40%CHF_3 have a r_{ms} of 19 nm



(a)



(b)

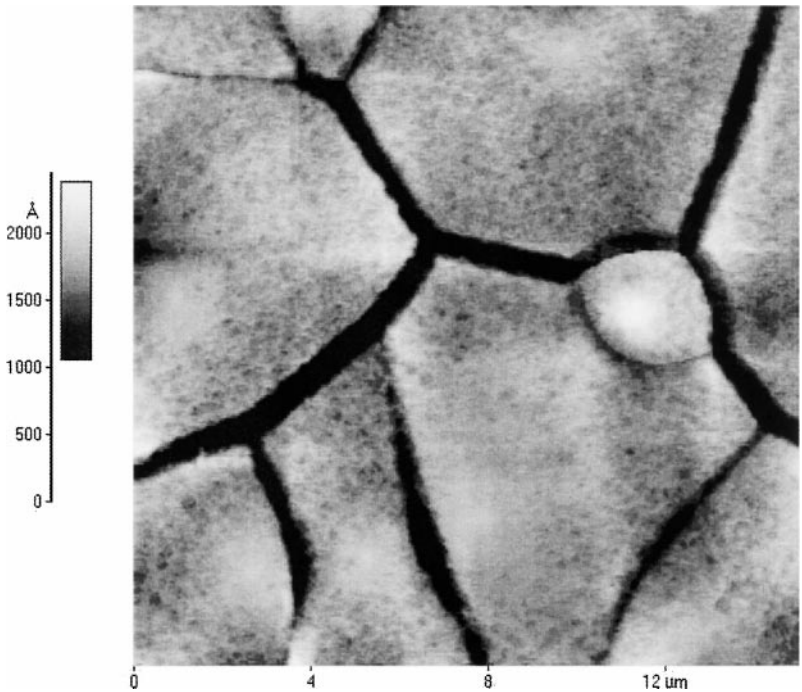
Figure 3. Etch rate for a gas mixture 60%Ar/40%CHF_3 (a) as a function of the acceleration voltage (current density = 0.7 mA/cm^2) (b) as a function of the current density (acceleration voltage = 800 V).

in comparison with a r_{ms} around 4 nm for unetched PZT films. However, The roughness is more important under the same conditions of etching (acceleration and current density) for pure argon ion beam (Fig. 4a) than still CHF_3 reactive gas.

We observe a preferential etch at the grain boundaries in Fig. 4a. This behavior is probably the result of two combined phenomena. A composition variation between the grain and the boundary and/or a lateral etching inducing a boundary widening could add to the etching process. It is well known in etch technology that the ion reflections from the feature sidewalls generates a so-called trenching phenomenon. This effect was also observed with reactive etchings, only for low concentration of CHF_3. For 40% of CHF_3 this

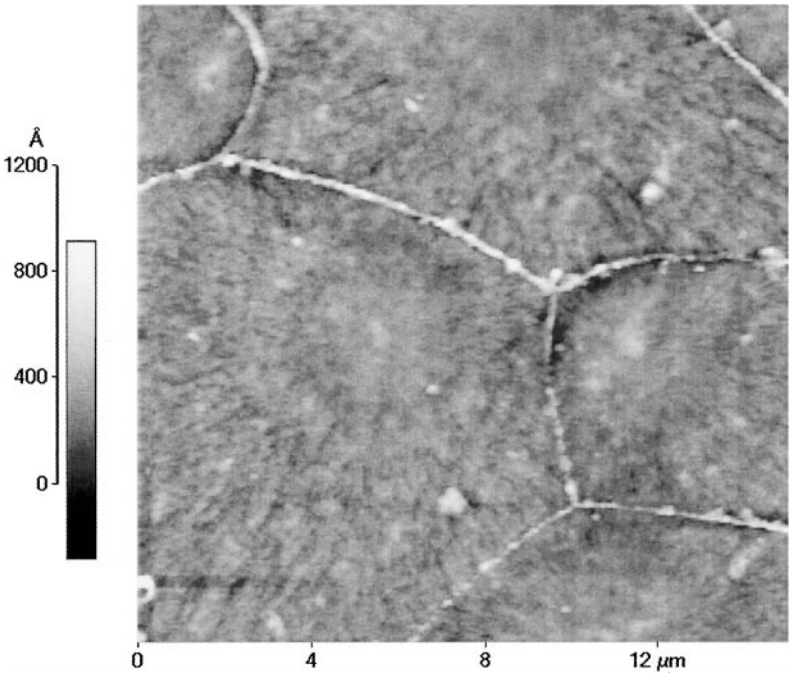
preferential etch disappear indicating a reduction of the physical effects of the bombardment largely compensated by chemical effects. Moreover when the proportion of CHF_3 increases one extra thickness is formed at the grain boundaries as the Fig. 4b shows it. We allot this effect to the formation of PbF_2 at the grain boundaries. This compound is all the more present since the concentration in CHF_3 is high, PbF_2 have a high boiling point. Ar irradiation onto the PZT surface preferentially breaks Pb—O bonds, releasing Pb in the crystal, which is subsequently fixed to F radical resulting in a high PbF_2 concentration at the grain boundaries. This is in accord with reference [8].

In addition, by comparison with pure Ar etching, the sidewall profiles can be improved by the simple fact of the strong selectivity, which exists between the photoresist and the PZT for 40% of CHF_3.



(a)

Figure 4. 15×15 μm AFM micrograhs of PZT etched at 800 V, 0.7 mA/cm^2 with: (a) pure Ar ion beam (b) Ar/CHF_3 60/40 ion beam. *(Continued)*



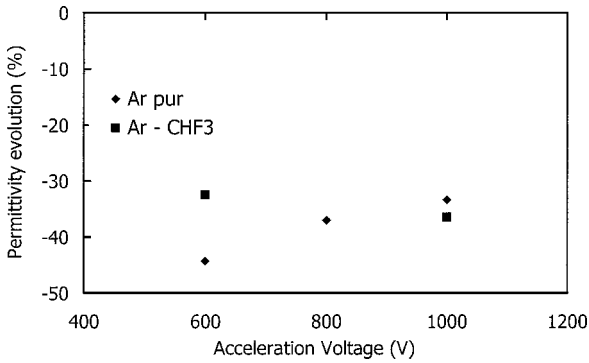
(b)

Figure 4. (Continued).

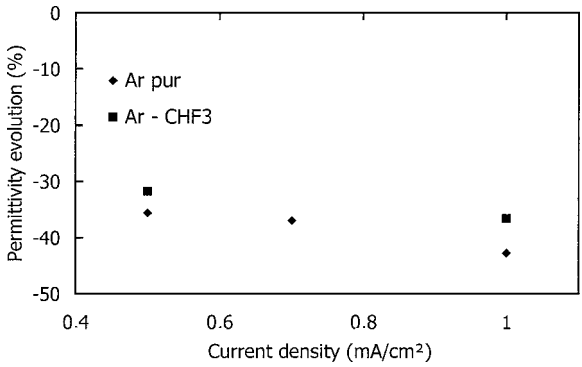
c) Dielectric and Ferroelectric Properties

Electrical properties of PZT films, after etching with pure Ar and Ar/CHF_3 gas mixture, have been compared by varying the acceleration voltage and the current density. As shown in Figs. 5a and 5b, the permittivity ε_r decreases after etching process.

The ε_r reduction could be explained by the presence of roughness, amorphized material, charged or neutral defects on the film surface and at the grain boundaries. This damage layer, present in surface, can be considered to have a lower permittivity than ferroelectric PZT and this can induce a smaller dielectric constant for the global structure. The improvement of the roughness observed during reactive etchings does not result in a broad evolution of the permittivity. The permittivity evolutions according to the acceleration voltage and the current density were described elsewhere [13] and the roughness seems not to be the predominant factor in the permittivity decreasing.



(a)



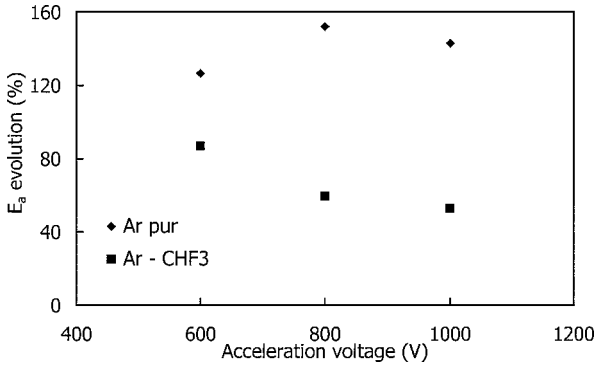
(b)

Figure 5. ε_r evolution as a function of: (a) current density (acceleration voltage = 800 V) and (b) acceleration voltage (current density = 0.7 mA/cm^2) with pure Ar ion beam and with Ar/CHF_3 reactive beam.

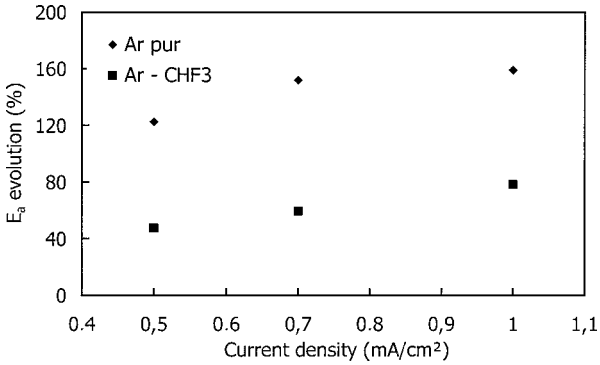
Therefore, the permittivity decrease could be linked to the domain wall pinning induced by defects.

The hysteresis loops measured after etching show a maximum polarization decreasing (between 15 to 25%) while the average remnant polarization is little modified. The very weak decrease of the remnant polarization suggests that an important pinning phenomenon occur, preventing the domain back switching.

After etching film and top electrode annealing, the average coercive field E_a is increased. E_a is defined as $E_a = (|E_c^+| + |E_c^-|)/2$. The magnitude of E_a was measured, as a function of discharge parameters such as current density



(a)



(b)

Figure 6. Average coercive field evolution as a function of: (a) current density (acceleration voltage = 800 V) and (b) acceleration voltage (current density = 0.7 mA/cm^2) with pure Ar ion beam and with Ar/CHF_3 reactive beam.

and voltage acceleration (Fig. 6). When acceleration voltage and current density increase, the average coercive field follows an evolution similar to the roughness ones. We suggest that the damage zone at the film surface is directly responsible for the E_a increase.

IV. CONCLUSION

In this work, we have presented results concerning the Ar and ion beam etching of PZT thin films. An important etch rate (95 nm/min) and selectivity

(7.5) can be achieve at 800 V and 0.7 mA/cm^2 for a gas ration of 60/40 (Ar/CHF_3).

We have shown that the maskless PZT etching generate a large number of damages in terms of surface morphology and electrical properties. Globally, the PZT roughness is largely higher after etching, whatever the etching parameters, and more especially, it increases more and more with increasing current density and acceleration voltage. We have also observed a widening of the grain boundaries; the grain boundaries are preferentially etched in pure Ar process. This effect is diminished when we increase the proportion of CHF_3.

When we have compared the electrical results after contact annealing, before and after etching, We have obtained the following evolution: the permittivity is particularly reduced, the maximum polarization decreases whereas the remnant polarization is only little modified, the average coercive field increases and finally the internal field remains practically unchanged.

REFERENCES

[1] S. Mancha, "Chemical etching of thin film PLZT," *Ferroelectrics* **135**, 131 (1992).

[2] T. Kawagughi, H. Adachi, K. Setsune, O. Yamazaki, and K. Wasa, "PLZT thin-film waveguides," *Appl. Opt.* **23**, 2187 (1984).

[3] K. Saito, J. H. Choi, T. Fukuda, and M. Ohue, "Reactive ion etching of sputtered $PbZr_{1-x}Ti_xO_3$ thin films," *Jpn. J. Appl. Phys.* **31**, L1260 (1992).

[4] D. P Vijay, S. B. Desu, and W. Pan, "Reactive ion etching of sputtered $PbZr_{1-x}Ti_xO_3$ thin films," *J. Electrochem. Soc.* **140**, 2635 (1993).

[5] W. Pan, S. B. Desu, K. Yoo In, and D. P. Vijay, "Reactive ion etching of $PbZr_{1-x}Ti_xO_3$ and RuO_2 films by environmentally safe gases," *J. Mater. Res.* **9**, 2976 (1994).

[6] S. Yokoyama, Y. Ito, K. Ishihara, K. Hamada, T. Ohnishi, J. Kudo, K. Sakiyama, "High temperature etching of PZT/Pt/TiN structure by high density ECR plasma," *Jpn. J. Appl. Phys.* **34**, 767 (1995).

[7] C. W. Chung and C. J. Kim, "Etching effects on ferroelectric capacitors with multilayered electrodes," *Jpn. J. Appl. Phys.* **36**, 2747 (1997).

[8] J. Baborowski, P. Muralt, N. Ledermann, E. Colla, A. Seifert, S. Gentil, and N. Setter, "Mechanisms of $Pb(Zr_{0,53}Ti_{0.47})O_3$ thin film etching with ECR/RF reactor," *Int. Ferr.* **31**, 261 (2001).

[9] N. Ikegami, T. Matsui, and J. Kanamori, "Dry-etching mechanism of sputtered $Pb(Zr_{1-x}Ti_x)O_3$ film," *Jpn. J. Appl. Phys* **35**, 2505 (1996).

[10] J. J. Van Glabbeek, G. A. C. M. Spierings, M. J. E. Ulenaers, G. J. M. Mans, and P. K. Larsen, "Reactive ion etching of $Pt/PbZr_xTi_{1-x}O_3/Pt$ integrated ferroelectric capacitors," *J. Mat. Res. Symp. Proc.* **310**, 127 (1993).

[11] G. Suchaneck, R. Tews, and G. Gerlach, "A model for reactive ion etching of PZT thin films," *Surf. and Coatings Technol.* **116–119**, 456 (1999).

[12] G. Velu, D. Rèmiens, and B. Thierry, “Ferroelectric properties of PZT thin films prepared by sputtering with stoichiometric single oxide target: comparison between conventional and rapid thermal annealing,” *J. Europ. Ceram Soc.* **17**, 1749 (1997).

[13] C. Soyer, E. Cattan, and D. Rèmiens, “Ion beam etching of lead-zirconate-titanate thin films: correlation between etching parameters and electrical properties evolution,” *J. Appl. Phys.* **92**, 1048 (2002).