ELSEVIER

Ceramics International 30 (2004) 1215–1218

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of microstructure on reactive ion etching of sol–gel-derived PZT thin film

Shi Peng*, Yao Xi

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Received 28 November 2003; accepted 22 December 2003

Available online 30 April 2004

Abstract

Micro patterning and etching characteristics of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin film are very interesting for the fabrication of various ferroelectric micro devices. Besides the effects of plasma, the microstructure of PZT films was very important in etching process. In this article, the characteristics of reactive ion etching (RIE) of PZT films with different microstructure were investigated. The morphology and microstructure were examined by atomic force microscopy (AFM) and X-ray diffraction (XRD). The properties of etching were measured by AFM and X-ray photoelectron spectroscopy (XPS). With the annealing temperature increased, the microstructure became more compact and the etching rate decreased. The highest etching rate was 13 nm/min when the microstructure of PZT film was amorphous.

Keywords: B. Microstructure; D. PZT; Thin film; RIE

1. Introduction

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) films had been studied for many applications such as ferroelectric random access memory (FeRAM), microelectro mechanical systems (MEMS), and pyroelectric detectors [1]. The fabrication of these devices required the development of etching processes for PZT films as well as deposition processes. Many studies had 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), in various gas mixtures involving chlorine- or fluorine-based gases [2–5].

In general, chlorine chemistries showed faster etching than fluorine chemistries, while the etch profiles could be varied depending on the etching conditions. A highly selective photoresist mask for the etching of PZT films in fluorine-based gases could be obtained, but etching residues like polymers were easily formed. On the other hand, chlorine chemistries generally exhibited clean etch profiles, but the selectivity was poor compared with the fluorine chemistries.

In this paper, the relationship between film structure and etching properties were researched in a reactive ion etching setup. The surface morphology and etching characteristics were investigated.

2. Experiment

The precursor solution was prepared to give a nominal stoichiometry of $Pb(Zr_{0.52}Ti_{0.48})O_3$. For the synthesis of PZT sols, tetrabutyl titanate ($Ti(OC_4H_9)_4$), lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$) and tetrabutyl zirconate ($Zr(OC_4H_9)_4$) were used as starting materials. Ethylene glycol monoethyl ether ($HOCH_2CH_2OC_2H_5$) was used as solvent. The solution was stabilized with acetylacetone ($CH_3COCH_2COCH_3$) and the concentration was 0.4 mol/l.

The PZT films were deposited on the Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates by spin coating. The substrates were prepared by sputtering and pre-annealed at 600 °C for 30 min to release the stress. Precursor solution was spun on the substrate at 3000 rpm for 20 s. The coated substrates were baked at 400 °C for 30 min before next deposition. The films with six layers were annealed at 450, 500, 550, 600, 650, and 700 °C for 1 h, respectively to form various structures and phases.

* Corresponding author. Fax: +86-29-82668794.
E-mail address: spxjy@mailst.xjtu.edu.cn (S. Peng).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.078

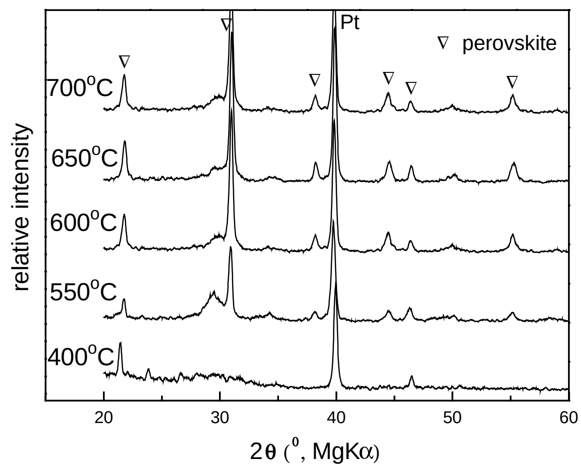

Fig. 1. XRD patterns of PZT with different annealing temperatures.

The etching process was carried out in a RIE setup. The etching samples were patterned using a conventional photoresists with standard lithographic process. The PZT films were etched using CHF_3/Ar plasma. The total CHF_3/Ar gases flow rate was 30 sccm, the radio frequency (RF) power was 150 W, and the ratio of CHF_3 to Ar was 70/30 in the plasma mixture.

The deposited PZT films were examined by X-ray diffraction (XRD). The surface states of each element in PZT film were examined by X-ray photoelectron spectroscopy (XPS). The etching rate and the morphologic characteristics of the film surface were investigated by atomic force microscopy (AFM).

3. Results and discussions

3.1. Microstructure of PZT films

3.1.1. XRD pattern

Fig. 1 shows the XRD pattern of PZT in different annealing temperatures. From the results, the PZT film was still amorphous when the final annealing temperature was 400 °C. The structure of PZT film was perovskite when the temperature was higher than 550 °C. The microstructure of the film became better with the increase of the annealing temperature.

3.1.2. Surface morphology

Fig. 2 shows the morphology characteristics of PZT films annealed at different temperatures. From the AFM images,

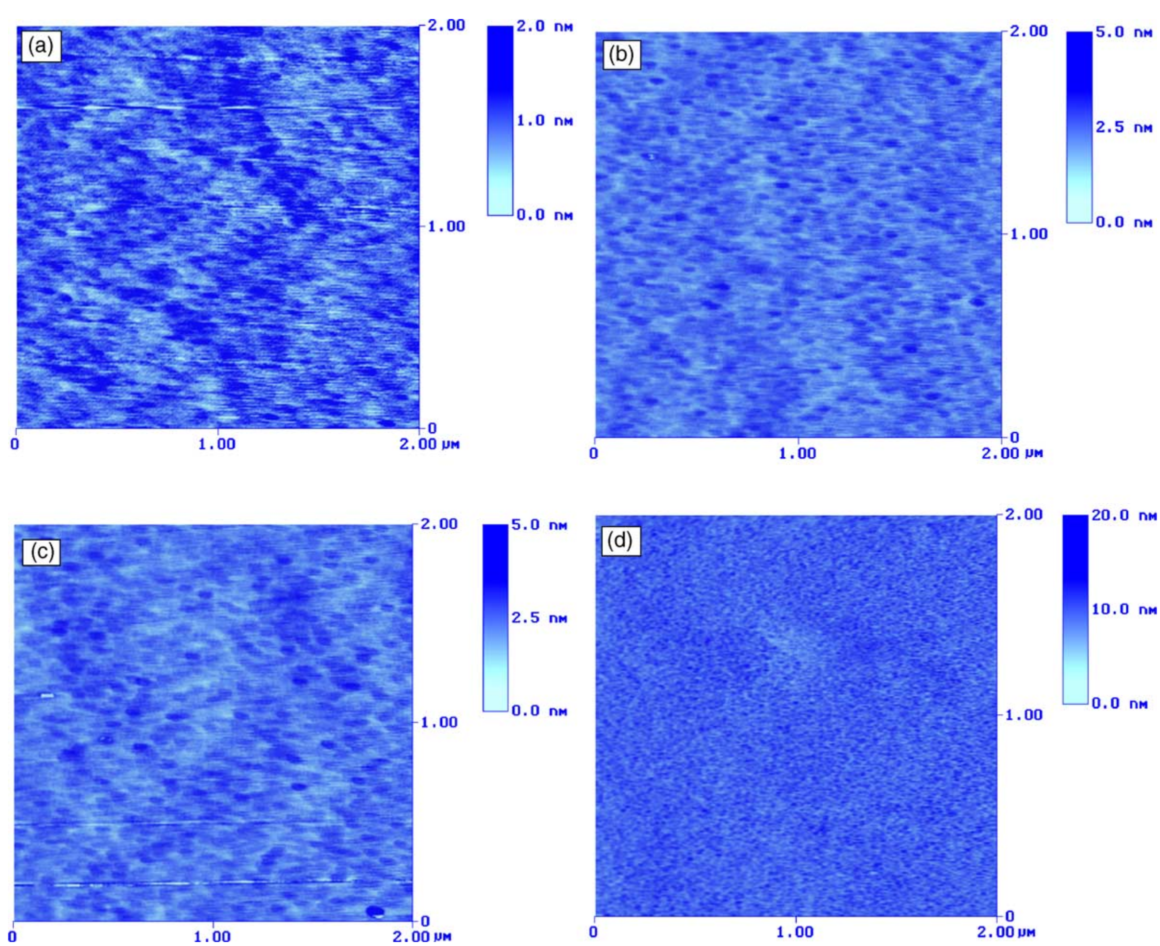

Fig. 2. AFM images of PZT films annealed at different temperatures: (a) 450 °C (b) 500 °C (c) 550 °C (d) 600°C.

Table 1
Surface roughness (nm) of PZT films with different annealing temperature

	450 °C	500 °C	550 °C	600 °C	650 °C
r_{ms}	0.202	0.25	0.275	0.772	0.813
I_{mg}Ra	0.157	0.199	0.215	0.607	0.634
$I_{mg}Z$	3.268	2.162	4.661	7.552	7.731

the surface structure of PZT films became compact and the homogeneity improved. The crystallinity became better also. The defects in the surface layer decreased. Moreover, the crystal boundaries of PZT film were enclosed by the continuous grain structure. When the film annealed at 600 °C the microstructure of PZT film is compact and the surface morphology is smooth. The crystallites were very small and compact.

However, the roughness was more important under the same conditions of etching for CHF_3/Ar reactive gases. The roughness of etched films was characterized by the r_{ms} (r_{ms} was defined as the root mean square). The results of surface roughness of etched films were shown in Table 1. The r_{ms} became bigger from 0.202 with 450 °C annealing to 0.813 with 650 °C. At the same time the I_{mg}Ra changes from 0.157 to 0.634 continuously.

According with the results of Baborowski, there was a preferential etch at the grain boundaries in the film [6]. This behavior was probably the results of two combined phenomena. A composition variation between the grain and

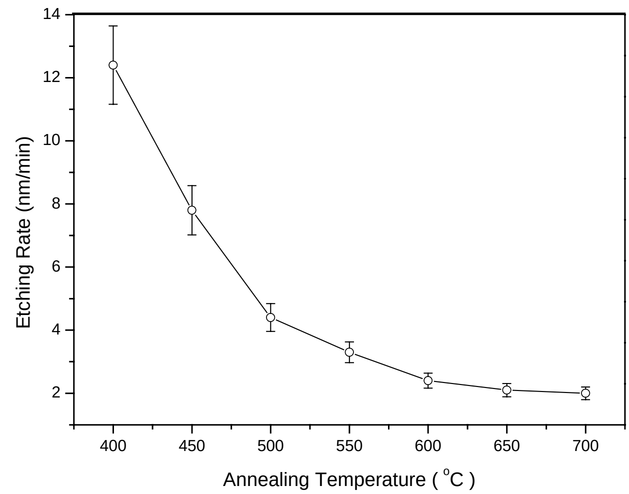

Fig. 3. Etching rate of PZT films with different annealing temperature.

the boundary and/or a lateral etching inducing a boundary widening could add to the etching process.

3.2. Etching characteristics

According to the principle of plasma deposition technology, the amount of attached incident plasma particles increased with the increase of deposition time. So the homogeneity of film surface became worse while the etching process. When the plasma energy was relative low, the

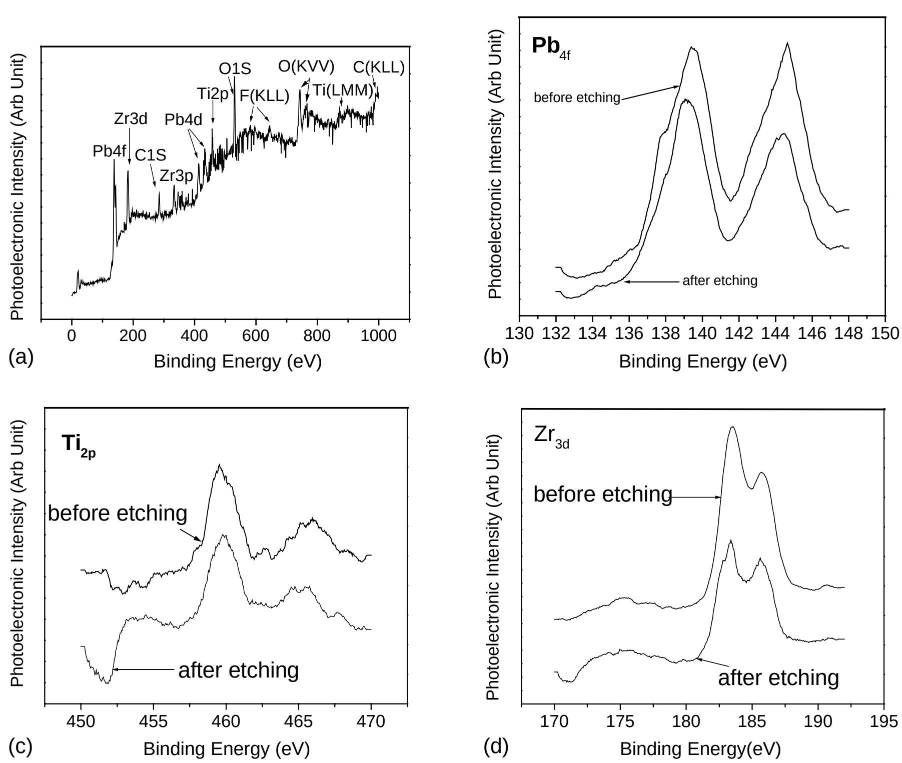

Fig. 4. XPS patterns of PZT film annealed at 600 °C: (a) survey scan of etched PZT film, (b) narrow-scan of Pb_{4f} before and after etching, (c) narrow-scan of Ti_{2p} before and after etching, (d) narrow-scan of Zr_{3d} before and after etching.

density of active ions and radicals were low. The etching mechanism of PZT film was the combination of chemical etching, ion assisted etching and physical bombardment. So the characteristics of surface layer were very important to the etching rate at the fixed etching condition, especially with lower RF power.

Fig. 3 indicates the etching rates of PZT films with different annealed temperatures. With the annealing temperature increased, the etching rate decreased. The reason was that the grain size became bigger and the density became compact with higher temperature annealing. When the temperature was higher than 650 °C, the etching rate is relatively stable. That is to say the grain size of surface layer was not the main factor to affect the etching rate.

On the other hand, the etching rate decreased with bigger grain size and well crystallized microstructure.

3.3. XPS patterns

Fig. 4 indicates the XPS patterns of PZT film annealed at 600 °C for 1 h before and after etching. The RF power of plasma is 150 W, the total flow rate of mixture gases is 30 sccm, and the ratio of CHF_3/Ar is 70/30. From the figures, we can find that the intensity of main peaks decreased after etching in the CHF_3/Ar plasma. It means that the bonds are destroyed by the ion bombardment and chemical interaction on the surface layer. On the other hand, the shifts of main peaks indicate the change of bonds by the vigorous bombardment effects. The effects of chemical reactions are not dominant. So the etching mechanism is bombardment dominating.

4. Conclusions

From the results and discussion above, the characteristics of surface layer and microstructure were very important to the etching behavior in RIE system. The etching mechanism was bombardment dominating. The highest etching rate is about 13 nm/min in our RIE setup in CHF_3/Ar plasma (RF power is 150 W, total gas flow rate is 30 sccm, the ratio of CHF_3 to Ar is 70/30, and the working vacuum is 1 Pa) when the PZT films were amorphous and annealed at 400 °C for 1 h. With the annealing temperature increased from 500 to 700 °C, the density of film increased as well as the microstructure became better. At the same time, the etching rate decreased continuously. The etching rate was relative higher when the thin film was amorphous and without crystallization. The grain size and the properties of crystal boundaries played an important role in the etching process.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 60377035), and the Ministry of Sciences and Technology of China through 973-project under grant 2002CB613305 and International Joint Research Project of China–Israel (time: 2002–2003).

References

[1] A. Ignatiev, Y.Q. Xu, N.J. Wu, D. Liu, Pyroelectric, ferroelectric and dielectric properties of Mn and Sb-doped PZT thin films for uncooled IR detectors, Mater. Sci. Eng. B56 (1998) 191–194.

[2] Y.J. Lee, H.R. Han, J. Lee, G.Y. Yeom, A study of lead zirconate titanate etching characteristics using magnetized inductively coupled plasmas, Surf. Coat. Technol. 131 (2000) 257–260.

[3] C.W. Chung, Y.H. Byun, H.I. Kim, Inductively coupled plasma etching of a $Pb(Zr_xTi_{1-x})O_3$ thin film in a HBr/Ar plasma, Microelectron. Eng. 63 (2002) 353–361.

[4] J.K. Jung, O.J. Lee, Dry etching character of PZT films in CF_4 and Cl_2/CF_4 ICPs, Jpn. J. Appl. Phys: Part 1 40 (3A) (2001) 1408–1419.

[5] Y.Y. Lin, Q. Liu, T.A. Tang, X. Yao, XPS analysis of PZT thin film after etching in CHF_3 plasma, Appl. Surf. Sci. 165 (2000) 34–37.

[6] J. Baborowski, P. Muralt, N. Ledermann, E. Colla, A. Seifert, S. Gentil, N. Setter, Mechanisms of $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin film etching with ECR/RF reactor, Integr. Ferroelectrics 31 (2001) 261–271.