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Single Grained PZT Array Fabricated by Physical Etching of Pt Bottom Electrode

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Ta-doped PZT thin films prepared by reactive co-sputtering method could be transformed into single grained perovskite structure utilizing physical etching of Pt bottom electrode. It is found that PZT perovskite phase on damaged (111) Pt electrode by IMD was more easily crystallized than random oriented Pt electrode and less crystallized than (111) Pt electrode. This shows that amorphized Pt electrode surface by IMD process has an effect on crystallization of PZT perovskite phase. 40 μm×40 μm square shape single grain PZT array could be obtained utilizing the difference of incubation time for nucleation of rosettes between ion damaged Pt and (111) oriented Pt electrode. Single grained PZT thin films show low leakage current density of 1×10^{-7} A/cm^2 and high break down field of 440 kV/cm. The loss of remanent polarization after 10^{11} cycles was less than 15% of initial value.

Key words: Single grain, Incubation time, Rosettes, PZT, Ion damage

I. Introduction

Ferroelectric memories are thought to be promising in future applications because of their nonvolatile characteristics, radiation hardness, high-speed operation, and the high integration using a simple structure.[1-3] Extensive studies have been concentrated on the ferroelectric materials, especially lead zirconate titanate families, and bismuth layer perovskites. However, there are still several problems that should be overcome to apply these materials to semiconductor devices, such as fatigue, high leakage current, imprint, and suitable metallization scheme for the ferroelectric capacitors.[4,5] So far due to its process simplicity, smooth surfaces, and high stability with ferroelectric material Pt has been widely used for the electrode material, however, with Pt electrode PZT shows poor fatigue endurance, which limits the lifetime of memory devices. Now, to solve these problems many studies are being carried out on the use of oxide electrode and fabrication of PZT single crystals. Yet, oxide electrodes such as RuO_2,[6] IrO_2,[7] LSCO[8] have some important issues in connection with PZT ferroelectric capacitor such as poor leakage current characteristics, surface morphology and so on. On the contrary, PZT single crystal shows superior characteristics, but it requires the single crystal substrate in fabrication process, which is impossible in integration with Si.[9]

It is well known that PZT perovskite phases nucleate in a pyrochlore matrix as rosettes which have single crystallographic orientation,[10] and it has been reported of successful fabrication of single grained array using selective nucleation and growth by Joo *et al.*[11] In this study we developed new fabrication process of PZT single grained array by physical etching of Pt bottom electrode. The mechanism of formation of single grained array was investigated and electrical properties were measured in comparison with poly-grains.

II. Experimental Procedure

Pt bottom electrodes of 3,000 Å were prepared by RF

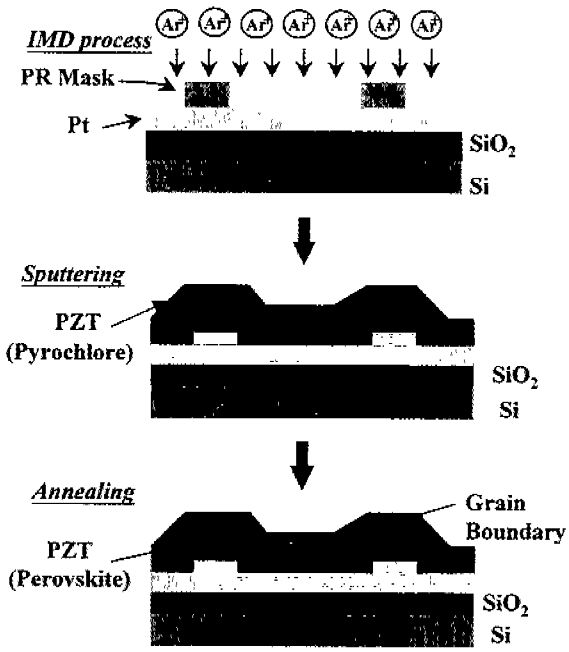

Fig. 1. Fabrication process of single grained PZT array by selective bottom electrode etching.

magnetron sputtering on SiO_2(5,000 Å)/Si substrates. Photoresist structures of various sizes and spaces were patterned on the Pt electrode by conventional optical lithography. Fig. 1. shows the schematic diagram of IMD (Ion Mass Doping) process for the physical etching of Pt bottom electrode. Pt bottom electrode was etched with Ar ion accelerated in one direction by D.C. voltage grids. Acceleration voltage in IMD process was 15 kV, and working pressure was 1×10^{-4} Torr.

Ta-doped PZT thin films were formed on patterned Pt/SiO_2/Si substrates by reactive co-sputtering at 350°C using multiple metal target of Pb, [Zr,Ta], Ti. Base pressure before sputtering was below 1×10^{-5} Torr and the working pressure was 20 mTorr during sputtering. The crystal structures of the films were investigated with X-ray diffractometer. The conduction properties were measured using HP4140B pA meter and the dielectric properties were examined by RT66A. Fatigue test was performed at room temperature with a square pulse of ±10 V at 1 MHz.

III. Results and Discussion

Fig. 2 shows the variation of grain size with annealing time and groove height. PZT thin films were annealed in a tube furnace at 650°C in air, and rosette sizes were observed by optical microscope. The grooves were 10 μm×10 μm sized square shapes and spaces between grooves were constant of 50 μm. The slope shows the grain growth rate. Growth rate was independent of groove heights in initial stage and decreased with grain growth. In case of 200 Å, 500 Å groove height, rosettes nucleated randomly and the grain arrays became like polycrystalline. And that transformation time to perovskite phases was shorter than that of higher groove heights. From this result, it is thought that the higher groove height was, i.e. the deeper the etching depth was, the more nucleation was depressed due to ion damage on Pt electrode. To confirm this result, we investigated the variation of incubation time with groove height and this is shown in Fig. 3. The incubation time was increased with increasing groove height and saturated with constant value at some groove height of above 1,000 Å.

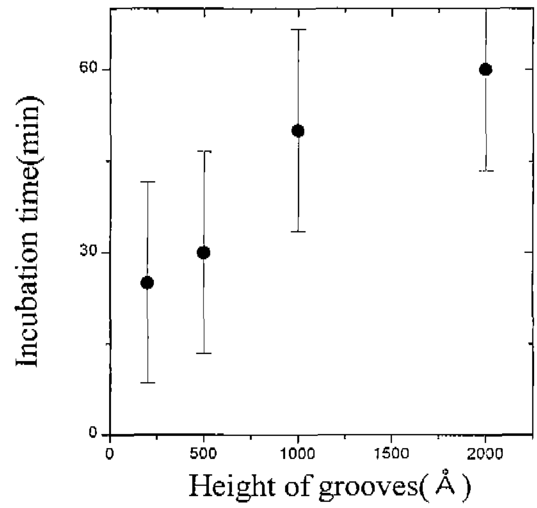

Fig. 3. Variation of incubation time with groove height. Annealing temperature is 650°C.

Fig. 4 shows the variation of grain growth rate with spaces between grooves. Growth rate was calculated from the growth length obtained after 20 minutes annealing. The nucleation sites were selected by grooves of 1,000 Å height. The growth rate was independent of spaces between grooves as shown Fig. 4. From Fig. 2 and Fig. 4 it can be noticed that the residual stress which may be generated at groove site has no effect on phase transformation.

Although the rosette growth rate was constant independent of groove height, nucleation rate was depressed as the etching depth was increased. Utilizing this difference of incubation time, single grain arrays could be formed in 40 μm spaces.(Fig. 5) When the spaces between grooves were lager than 40 μm, the time for impingement of laterally

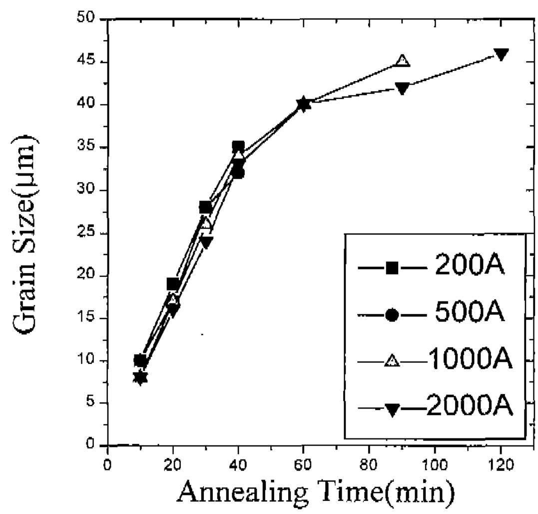

Fig. 2. Variation of grain size with annealing time and groove height. Annealing temperature is 650°C.

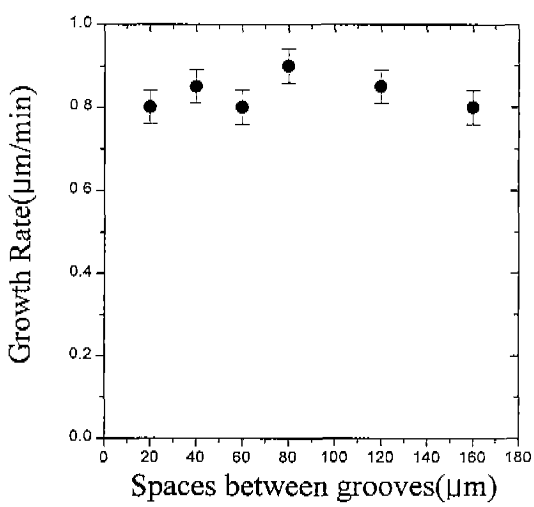

Fig. 4. Variation of grain growth rate with spaces between grooves. Annealing temperature is 650°C and groove height is 1,000 Å.

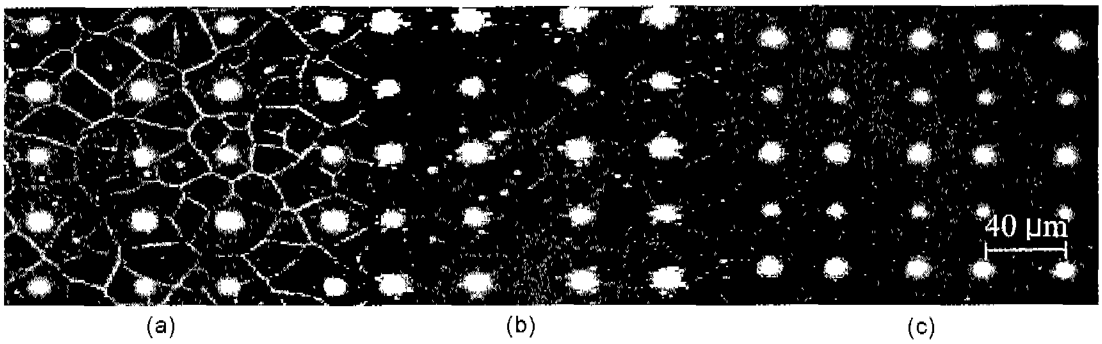

Fig. 5. Optical micrographs showing alignment of grain boundaries with different groove height : Groove height is (a) 200 Å, (b) 500 Å and (c) 1,000 Å respectively.

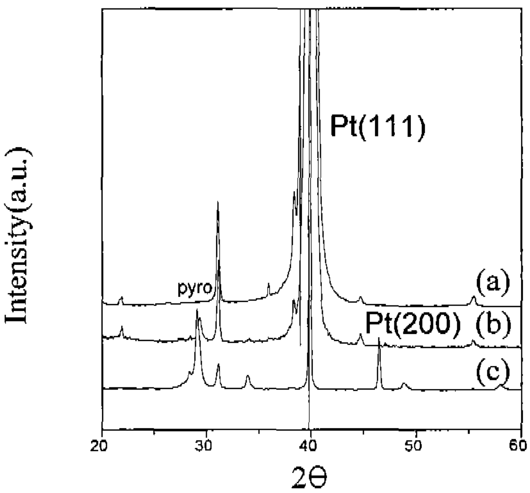

Fig. 6. XRD patterns of PZT thin films deposited on (a) (111) preferred oriented Pt, (b) ion bombarded Pt and (c) random oriented Pt electrodes respectively. The samples were annealed at 700°C for 5minutes.

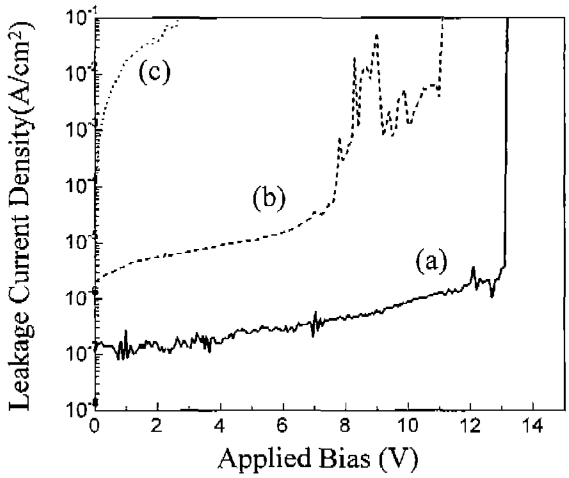

Fig. 7. Variation of I-V characteristics with the number of grain boundaries crossing the top electrode; (a) single grain (b) one grain boundary and (c) more than two boundaries.

grown grains became longer than the incubation time of the other region and resulted in nucleation at the other sites. Consequently, the formation of single grain array was impossible and the grain array became like a polycrystalline. This shows that the growth rate and incubation time in ion damaged region decide the grain size in single grain array. In this study, single grain array could be obtained stably in 40 μm groove spaces.

It seemed that the surface energy change of Pt electrode by ion bombardment caused increasing of the incubation time for nucleation in perovskite phase. To prove this, we compared crystallization temperature of PZT thin films deposited on differently manipulated Pt electrodes. Generally, Pt has (111)-preferred orientation in normal sputter-deposition condition, but in case of small addition of O_2 with Ar during sputtering, Pt lose the preferred orientation. In this way, Pt electrodes of (111) preferred orientation, random orientation and ion bombarded by IMD(Ion Mass Doping) were prepared. PZT thin films were deposited on these different Pt electrodes and annealed with constant temperature and time. Fig. 6 shows the XRD patterns of PZT annealed at 700°C for 5 minutes with different Pt electrodes. Crystallization was easily completed on (111)-preferred oriented Pt electrode and thus formed PZT perovskite phase had more intensive (111) peak as shown in Fig. 6. The PZT on damaged (111) Pt electrode by IMD was more easily crystallized than that on randomly oriented Pt electrode and less crystallized than that on (111) Pt electrode. This result shows that amorphized Pt electrode surface by IMD process has an effect on crystallization of PZT perovskite phase.

We compared electrical properties of single grained PZT thin films formed by grooved Pt bottom electrode with that of poly-grained PZT thin films. The variation of I-V characteristics with the number of grain boundaries crossing the top electrode is shown in Fig. 7. It shows the same electrical characteristics with poly-grains as the number of grain boundaries crossing the top electrode increases. The leakage current characteristics of single grain were very different from poly-grains. In poly grains, leakage current was rapidly increased as the applied voltage increased. But in single grains low leakage current density of 1×10^{-7} A/cm^2 was maintained to 333 kV/cm and break down occurred at the high field of 440 kV/cm.

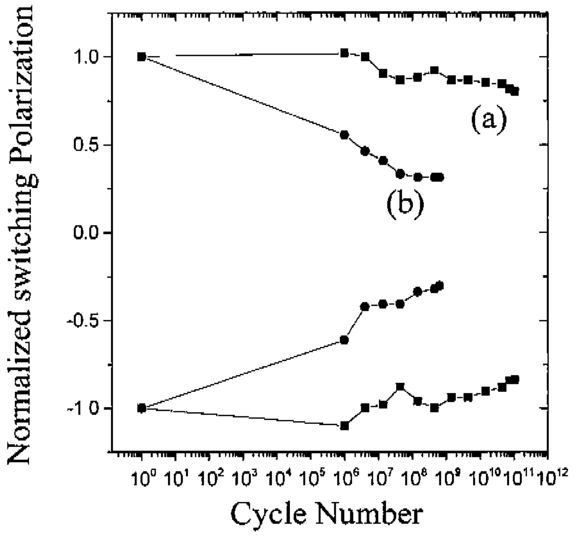

Fig. 8. Comparison of fatigue characteristics of (a) single grained PZT thin films with (b) poly-grained films.

Fig. 8 shows the fatigue characteristics of poly grained and single grained PZT thin films. In fatigue characteristics, degradation was not severe in single grained PZT thin films even after 10^{11} cycles while the poly-grains degraded rapidly over 10^6 cycles.

IV. Conclusions

Single grained PZT thin films could be obtained using physical etching of Pt bottom electrode. The incubation time was increased with increasing groove height and saturated with constant value at some groove height of above 1,000 Å. It was found that amorphized Pt electrode surface by IMD process depresses the nucleation of PZT perovskite phase. 40 μm×40 μm square shaped single grain PZT array could be obtained utilizing the difference of incubation time for nucleation of rosettes between ion damaged region and undamaged region of Pt electrode. Single grained PZT thin films show low leakage current density of 1×10^{-7}A/cm^2 and high break down field of 440 kV/cm. The loss of remanent polarization after 10^{11} cycles was less than 15% of initial value.

References

1. J. F. Scott and C. A. Araujo, Ferroelectric Memories, *Science*. **246**, 1400-1405 (1989).
2. J. Carrano, C. Sudhama, J. Lee, Al Tasch, W. Shepherd and N. Abt, Electrical and Reliability Properties of PZT Thin Films for ULSI DRAM Applications, *IEEE Trans. Ultrasonic, Ferroelectrics and Frequency Control*, **38**(6), 690-703 (1991).
3. S. Sinharoy, H. Buhay, D. R. Lampe and M. H. Francombe, "Integration of Ferroelectric Thin Films into Nonvolatile Memories," *J. Vac. Sci. Tech. A*, **10**(4), 1554-1561 (1992).
4. J. Chen, M. P. Harmer and D. M. Smith, "Polarization Fatigue in Perovskite Ferroelectric Ceramics and Thin Films," *Proceeding of 4th International Symposium on Integrated Ferroelectrics*, 111-115 (1990).
5. M. V. Raymond, J. Chen and D. M. Smith, "Degradation of Ferroelectric Thin Films:A Defect Chemistry Approach," *Integrated Ferroelectrics*, **5**, 73-78 (1994).
6. H. N. Al-Shareef, K. R. Bellur, A. I. Kingon and O. Auciello, "Influence of platinum interlayers on the electrical properties of $RuO_2/Pb(Zr_{0.53}Ti_{0.47})O_3/RuO_2$ capacitor heterostructures," *Appl. Phys. Lett.*, **66**(2), 239-241 (1995).
7. T. Nakamura, Y. Nakao, A. Kamisawa and H. Takasu, "Preparation of $Pb(Zr,Ti)O_3$ thin films on electrodes including IrO_2," *Appl. Phys. Lett.*, **65**(12), 1522-1524 (1994).
8. H. N. Al-Shareef, B. A. Tuttle, W. L. Warren, D. Dimos, M. V. Raymond and M. A. Rodriguez, "Low Temperature Processing of Nb-doped $Pb(Zr,Ti)O_3$ Capacitors with $La_{0.5}Sr_{0.5}$-CoO_3 electrodes," *Appl. Phys. Lett.*, **68**(2), 272-274 (1996).
9. C. M. Foster, G.-R. Bai, R. Csencsits, J. Vetrone and R. Jammy, "Single-crystal $Pb(Zr_xTi_{1-x})O_3$ Thin Films Prepared by MOCVD : Systematic Compositional Variation of Electronic and Optical Properties," *J. Appl. Phys.*, **81**(5), 2349-2357 (1997).
10. S. Seraphin, D. Dhou, G. Teowee, J. M. Boulton and D. R. Uhlmann, "Transmission Electron Microscopy of PZT thin Films Prepared by a Sol-gel Technique," *Mat. Res. Soc. Symp. Proc.*, **310**, 369-374 (1993).
11. J.-H. Joo and S.-K. Joo, "Fabrication and Characterization of the Single Grained PZT Thin Film," *Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials*, 512-514 (1995).