Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 512-514

Fabrication and Characterization of the Single Grained PZT Thin Film

Jae-Hyun Joo and Seung-Ki Joo

Dept. of Metallurgical Eng. Seoul Nat'l Univ.
San 56-1 Shinlim-dong, Kwanak-ku, Seoul, 151-742, KOREA

PZT thin film devices suffer from the fatigue, aging and the high leakage current. These problems are mostly caused by the grain boundaries of the polycrystalline PZT thin films. In this work, elimination of the grain boundary was attempted by controlling the nucleation process of the perovskite phase and the electrical properties of the single grained PZT thin films were investigated. With proper control of the nucleation sites, the rosette type of a single grain as large as about 50μm could be obtained. The single grained PZT films show an excellent conduction properties ($J_{LC}=10^{-8}A/cm^2$, $E_{BD}=500kV/cm$.) and abnormal high dielectric constant (~12,000).

1. INTRODUCTION

Since PZT($PbZr_xTi_{1-x}O_3$) material shows an excellent piezoelectric, pyroelectric and ferroelectric properties, it has been used for many applications such as SAW(Surface Acoustic Wave), electro-optic device and actuator etc. Recently, much effort has been focused on the applications of memory devices such as FRAM(Ferroelectric Random Access Memory) and DRAM(Dynamic Random Access Memory)[1,2]. In these applications, current PZT thin films can not be used due to many problems such as the fatigue, aging and the high leakage current. It has been known that the grain boundary is mainly responsible for these problems[3]. In this work, single grained PZT thin films were prepared by controlling the nucleation site for the crystallization during RTA(Rapid Thermal Annealing) process. A ferroelectric device was made with the single grained PZT film and the electrical properties were characterized.

2. EXPERIMENTAL

Ta-doped PZT films(3000Å) were deposited on the $Pt/SiO_2/Si$ substrate by the co-sputtering method. The sputtering conditions are summarized in Table I. The RTA process using the halogen lamp was carried out to crystallize the films to the perovskite structure. Array of platinum thin film dots(10μm×10μm) was formed on the top of PZT thin films before the crystallization by the lift-off process. These Pt dots were supposed to work as seeds for the crystallization during RTA process because the temperature of the platinum dots is higher than that of the PZT thin film as illustrated in Fig. 1. The film composition was analyzed with EDS(Energy Dispersive Spectroscopy). The conduction properties of the films were measured by HP4140B pA meter. The dielectric properties were examined by IM5d impedance analyzer.

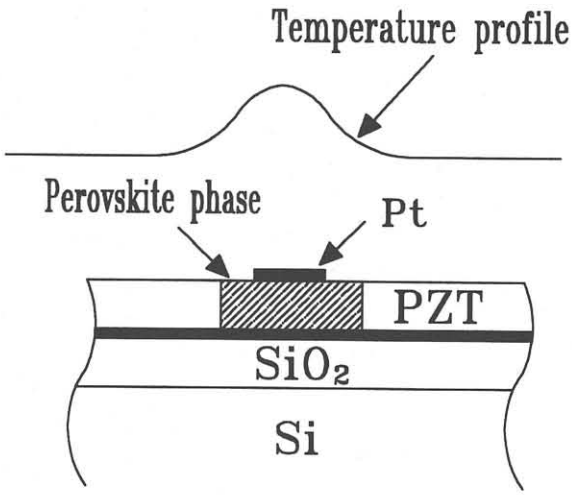


Fig. 1. The schematic diagram of the RTA process. The Pt top electrodes are supposed to work as seeds for the crystallization due to the difference in the profile.

Table I. Sputtering conditions

Substrate		Pt(100nm)/SiO_2(500nm)/Si
Substrate temperature		350℃
Gas flow		Ar(2sccm)+O_2(18sccm)
Pressure		20 mtorr
Power	Pb	DC 320V
	[Zr,Ti]	RF 300W
	Ta	DC 280V

3. RESULTS AND DISCUSSION

The composition of the sputtered PZT films was Pb/(Zr+Ti)~1.2, Zr/(Zr+Ti)~0.7 from EDS analysis. Fig. 2 shows the typical transformation pattern of the PZT thin films during RTA. It can be noticed from Fig. 2 that the perovskite phase is generated from the pyrochlore phase in a form of rosette. These rosettes grow as the transformation progressed and then impinged each other to form grain boundaries.

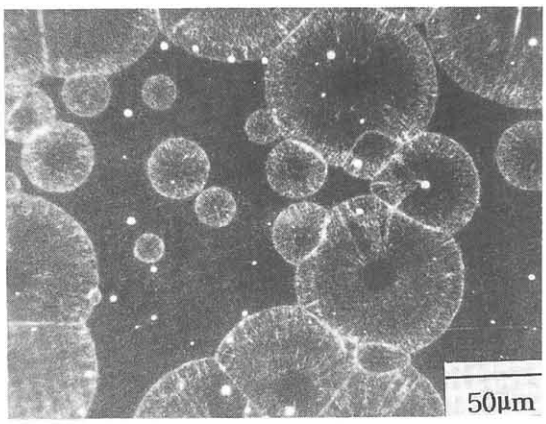


Fig. 2. Optical micrograph of Ta 1.8 at% doped PZT thin film annealed at 700℃ for 15sec. Rosette of the perovskite structure can be seen.

Fig. 3 is the scanning electron micrograph of the PZT film after the hard breakdown with a constant voltage. White circles in Fig. 3 indicate the place where the breakdown occurred. It is obvious from Fig. 3 that the grain boundary is mainly responsible for the high leakage current and low breakdown field of the PZT film. To eliminate such grain boundary effects, we have tried to fabricate the device on the single grain(rosette) PZT film where a controllable large grain required. When tantalum was doped to the PZT films, the nucleation rate of the rosette was depressed while the growth rate was increased[4]. Therefore, Ta-doped PZT films have abnormally larger grains than the undoped PZT films. Fig. 4 shows the effect of tantalum doping on the grain of the PZT film, where significant enlargement of the grain size can be seen. Fig. 5 shows the optical micrograph of the Ta-doped PZT film after RTA at 700℃ for 2min, where 10 μm×10μm platinum dots were placed at the top in 50μm space. The seeding effect of the Pt dots during the RTA process can be clearly seen in this figure. The rosettes were formed around the Pt dots and faced to each other at the grain boundaries so that square grains were formed after RTA process.

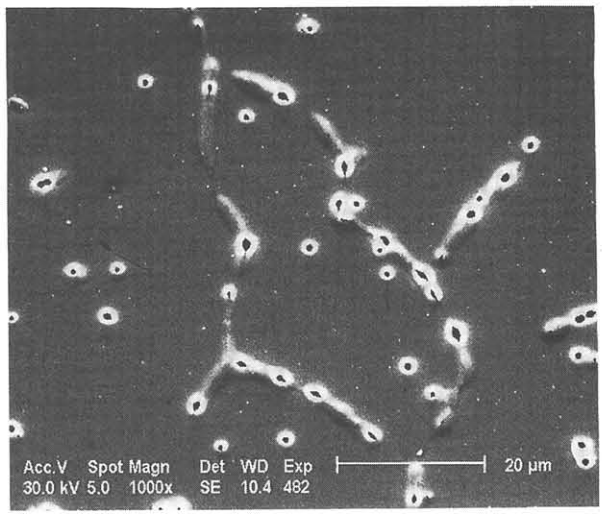
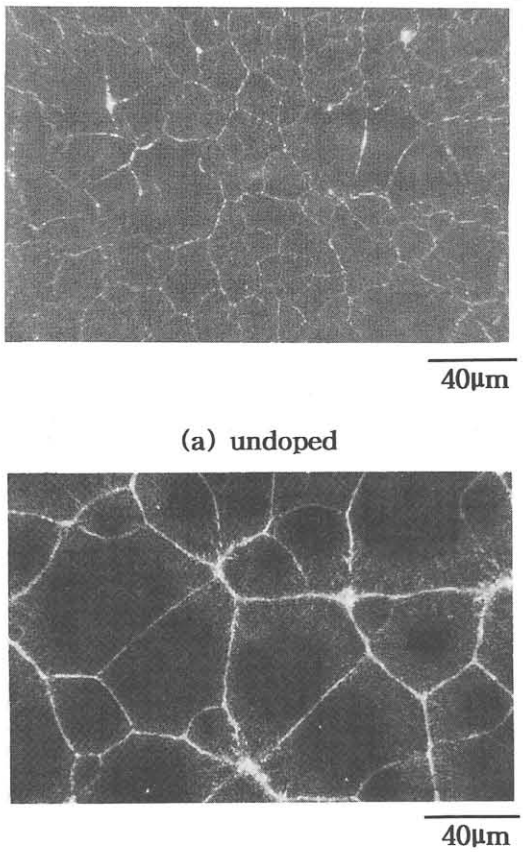


Fig. 3. Scanning electron micrograph of the Pt/PZT/Pt surface after the hard breakdown. It can be seen that the breakdown occurred along the grain boundaries of the PZT thin film.



(a) undoped

(b) Ta 1.8 at% doped

Fig. 4. Effect of tantalum doping on the grain size of the PZT thin film after annealing at 750℃ for 30sec by RTA.

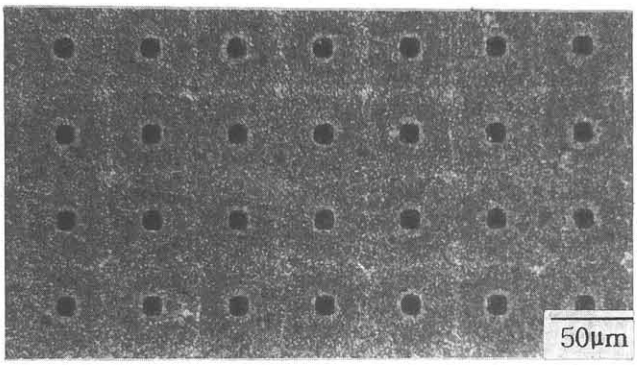


Fig. 5. Optical micrograph of Ta doped PZT film annealed at 700℃ for 2min. The Pt top electrode was deposited on PZT film by the lift-off process before the RTA process. Square shaped rosettes centered by the Pt dots can be seen.

I-V(Current-Voltage) characteristic of each rosette is shown in Fig. 6, where that of polygrained PZT films is compared. The polygrained PZT film shows gradual increase of the leakage current with an applied field, while single grained film shows much lower leakage current about 1×10^{-8}A/cm^2 and a hard breakdown at 500kV/cm. These values are significantly improved in comparison with other results. As can be seen in Fig. 7, the dielectric constant of the single grained PZT is about 12,000 at all frequencies, while polygrained PZT shows about 800. The dielectric constant of the single grained PZT is much larger than even that of the bulk PZT which is known to be about 1500[5].

4. CONCLUSION

We have successfully fabricated a single grained PZT film by proper control of the nucleation site of the perovskite phase. And the electrical properties of the single grained PZT thin film was characterized for the first time. The grain size of the Ta-doped film was abnormally larger than that of the undoped film after RTA. The perovskite phase of the rosette type could be selectively nucleated under the Pt top electrode by the RTA process. The single grained PZT films showed an excellent conduction properties(J_{LC}=1×10^{-8}A/cm^2) and dielectric constant ($\varepsilon r\sim12,000$)

5. ACKNOWLEDGEMENT

The publication cost has been supported by the Korea Science and Engineering Foundation through the Research Center for Thin Film Fabrication and Crystal Growing of Advanced Materials in Seoul National University.

6. REFERENCE

1) G. J. M. Dormans, P. K. Larsen, G. A. C. M. Spierings, J. Dikken, M. J. E. Ulenaers, R. Cuppens, D. J. Tayor, R. D. J. Verhaar, Integrated Ferroelectrics 6 (1995) 93.
2) H. Miki, Y. Ohji, Jpn. J. Appl. Phys. 33 (1994) 5143.
3) K. Okazaki and M. Nagata, J. Am. Ceram. Soc. 56(2) (1973) 82.
4) J. H. Joo and S. K. Joo, MRS 95 (submitted)
5) B. Jaffe, W. R. Cook, H. Jaffe : *Piezoelectric Ceramics* (Academic Press, New York, 1971) p.135.

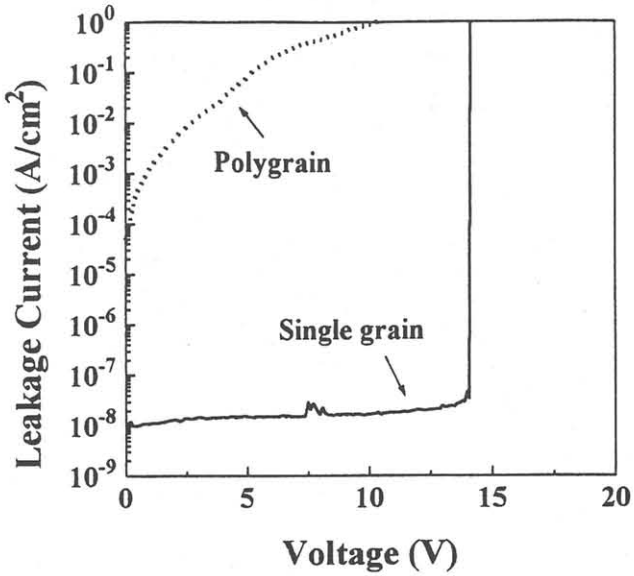


Fig. 6. Comparison of the current vs. voltage curve between the single grained and polygrained PZT films.

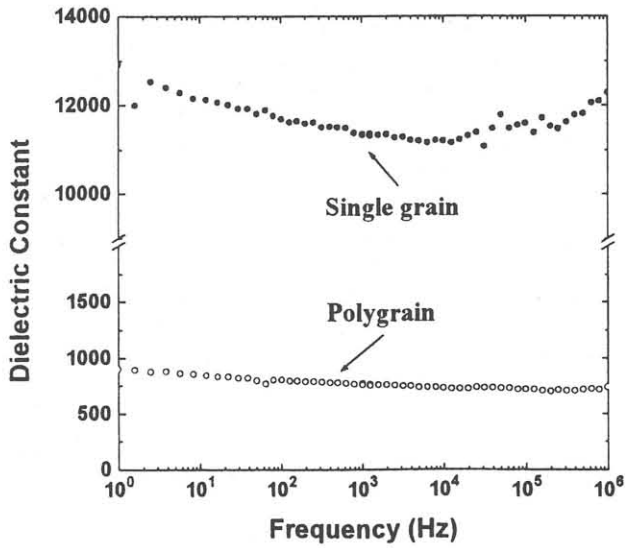


Fig. 7. Dielectric properties of the polygrained and single grained PZT film with at different frequencies.