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Quasi-Epitaxial Growth of PZT Thin Film to Fabricate Capacitor Suitable for 256Mb DRAM and Beyond

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Quasi-epitaxial PZT films were successfully grown on (111)oriented poly-crystalline Pt layer using two step processes by low temperature reactive sputtering and Rapid Thermal Annealing. Important factors to fabricate the PZT films were revealed as controls of target-substrate gap in sputtering apparatus, Pt surface condition and stoichiometric Pb-composition. The quasi-epitaxial PZT films above 65nm-thickness showed so improved electrical properties as 0.4nm-equivalent SiO_2 thickness with very low leakage current which are suitable 256Mb DRAMs and beyond.

1. INTRODUCTION

Lead-Zirconate-Titanate (PZT) thin films with high dielectric constant has been extensively investigated in view of its applications to 256Mb DRAMs and beyond with simple stacked capacitor. Therefore, sol-gel process,[1] metalorganic decomposition,[2] reactive sputtering,[3] laser ablation,[4] metalorganic chemical vapor deposition[5] and so on has recently been attempted, aiming at fabrication of PZT thin films with good dielectric properties. It has been recognized that control of Pb composition in the film should be precisely optimized, however, the control using high temperature growth process is more difficult than that by low temperature growth for the high vapor pressure of Pb element around the temperatures.[6] Thus, low temperature reactive sputtering can easily control not only total Pb composition but also the uniform composition in the depth, as already described elsewhere.[7] However, the electrical properties, especially leakage current, were degraded even on the Pb-controlled film thinner than 100nm.

The purpose of this paper is to describe Quasi-Epitaxial growth of PZT thin film onto (111)Pt to improve electrical properties under 100nm-thickness.

2. EXPERIMENTAL

PZT thin films were prepared at 350°C by conventional RF (13.56MHz) magnetron sputtering using multielement metal target as shown in fig.1. Pb-composition was conveniently controlled by Pb-pellet arrangement. Detailed growth conditions is shown on table 1. XRD patterns shows the PZT films grown at 350°C had a pyrochlore phase, therefore, the films were recrystallized to perovskite phase by Rapid Thermal Annealing (RTA) at 600°C. Detailed RTA condition were already described elsewhere.[8] 60nm-thick Pt layer with (111)oriented polycrystalline grains was grown on thermally oxidized Si wafer as substrate. DC-sputtered W was deposited on the PZT film as top electrode for electrical measurements.

X-ray diffraction (XRD) and scanning electron spectroscopy (SEM) were used to investigate crystallographic properties, inductive coupled argon plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence spectroscopy (XRFS) revealed compositional ratio of the PZT films, and RT66A ferroeletric tester from Radiant Technology and HP-4140A were used to measure D-E hysteresis loops and I-V characteristics.

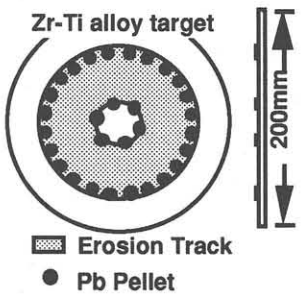

Fig. 1 Multielement metal target structure.

Table 1 Low temperature sputtering conditions.

Growth temperature	350 °C
Induced RF power	2W/cm²
RF frequency	13.56MHz
Growth pressure	4mtorr
Target-Sub. distance	90mm
Growth rate	6nm/min.

3. RESULTS AND DISCUSSIONS

ICP-AES showed that the Zr/Ti atomic ratio of as-grown PZT films were 45/55 in this case using Zr/Ti=48/52 alloy target. Decrease in Pb-compositional ratio after crystallization anneal as reported on sol-gel process[9] was not detected by ICP-AES and XRFS on annealed PZT films compared to the as-grown films as described elsewhere.[8] Therefore, the Pb-compositional ratio is optimized on as-grown film around stoichiometric composition as shown in fig. 2. XRD peak intensity of (111)perovskite was maximum around stoichiometric Pb-composition in contrast that the optimum Pb-compositional ratio that was around 20% excess Pb-composition in the case of high-temperature

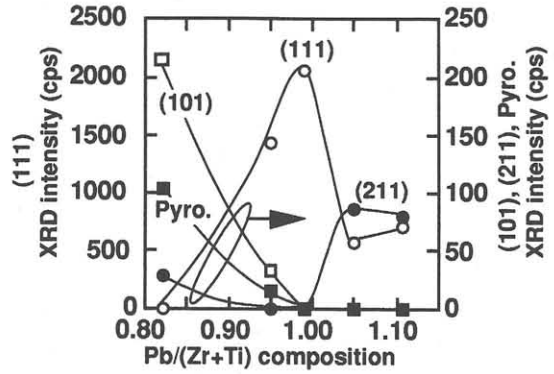

Fig. 2 XRD peak intensitiesof PZT films as a function of Pb-composition.

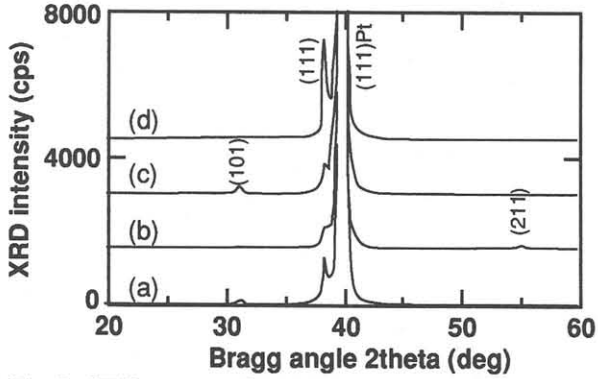

Fig. 3 XRD spectra of PZT films on various Pt layers.
(a) on as-deposited Pt layer.
(b) on annealed Pt layer in O2 at 800oC.
(c) on O2 plasma cleaned Pt layer.
(d) on Ar-plasma cleaned Pt layer.

sputtering growth.[11] However, the orientation of PZT film was influenced by Pt surface condition as shown in fig. 3. These XRD spectra showed that the PZT film grown on as-deposited Pt layer which was exposed in the air after Pt deposition was, however, almost oriented to (111), the other peak, for example (101), slightly observed on the film. On the other hand, the XRD peak intensities of PZT films grown on O2-annealed Pt layer and O2-plasma treated Pt layer were drastically decreased and the (211) or (101) peaks came to observed. In contrast to these aspects, the spectrum of fig. 3 (d) shows PZT film, which was grown on in-situ argon plasma cleaned Pt, was singly oriented to (111) on (111)Pt. Therefore, it will be concluded that the results of (a), (b) and (c) were caused by disordering of atom arrangement at the Pt layer surface and an origin of the disordering was caused by oxygen. The random oriented PZT films were also grown in narrow target-substrate (T-S) gap (40~50mm) as shown in ref. 10. In this case, it is speculated that some reactive species including of oxygen disordered Pt-atom arrangement at the Pt surface.

These controlled PZT layer, which was grown in wide T-S gap (90mm) after in-situ Ar-plasma cleaning on Pt-surface and optimized Pb-composition, was singly oriented to (111). Furthermore, FWHM of rocking curve on (111)PZT was wide, however, the FWHM was influenced by FWHM

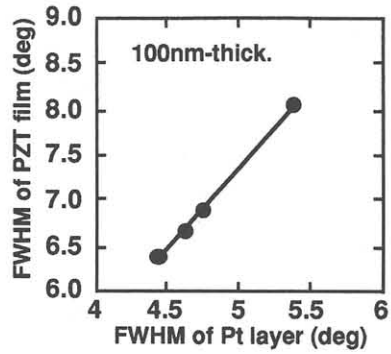

Fig. 4 FWHM of rocking curve on (111)PZT as a function of FWHM on (111)Pt.

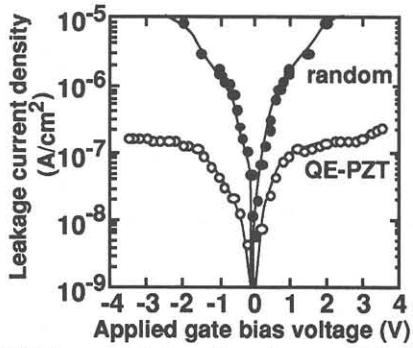

Fig. 5 I-V characteristics of random and QE-PZT films.

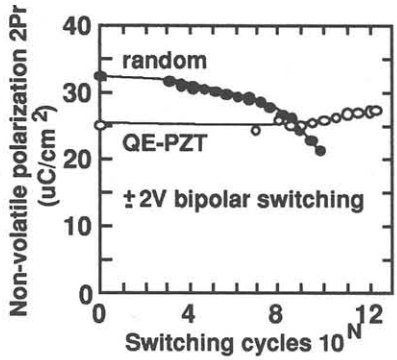

Fig. 6 Fatigue properties of random and QE-PZT films. (100nm-thick films)

of rocking curve on (111)Pt as shown in fig. 4. Therefore, it should be concluded that the PZT film was quasi-epitaxially grown on poly crystalline Pt layer.

The quasi-epitaxial (QE) PZT films has great merits for device applications. Figure 5 shows I-V characteristics of quasi-epitaxial PZT and random oriented PZT which was deposited narrow T-S gap. These two samples were 100nm-thick together and also treated by RTA. The leakage current of QE-PZT was drastically reduced compared to random PZT film. The leakage current density of QE-PZT was kept as low as 2×10^{-7}A/cm^2 at 3.5V. Figure 6 shows fatigue of 100nm-thick PZT films. Non-volatile polarization (2Pr) of the random oriented PZT film was reduced after bipolar switchings, however, no reduction of 2Pr was measured on QE-PZT film even after 10^{12} switch-

ings.

Figure 7 shows surface SEM images of QE (a) and random (b) PZT films after RTA. The QE-PZT has smooth surface in contrast to rough surface on random PZT film. The grain size of random PZT was around 40nm, however, grain boundary in QE-PZT was not clearly observed by TEM images. The mechanism of the difference between QE and random PZT surface has not been cleared, however, QE-PZT surface is suitable to fabricate thinner dielectric films.

Figure 8 shows I-V characteristics of 100nm- and 65nm-thick QE-PZT films. Leakage current was increased as decrease in the film thickness, however, the leakage current was kept as low as $2x10^{-7}A/cm^2$ even on 65nm-thick film. Figure 9 shows D-E hysteresis loops of 100nm- and 65nm-thick QE-PZT films. Polarization of the film was decreased as decrease in the film thickness, however, equivalent SiO_2 thickness was kept around 0.4nm. These electrical properties indicate the QE-PZT thinner films are suitable to fabricate capacitors drived in both Vcc-mode and Vcc/2-mode for 256Mb DRAMs and beyond.

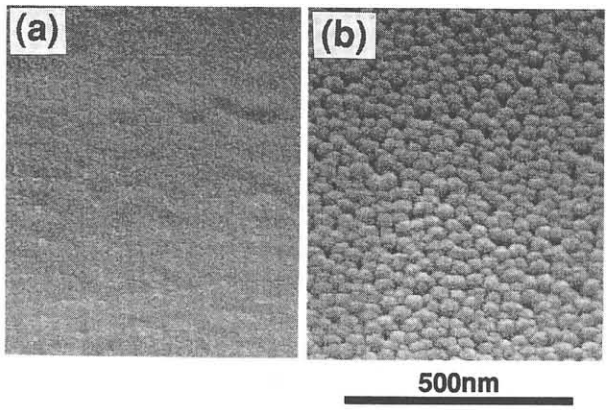

Fig. 7 SEM images of random (a) and QE (b)PZT films. (100nm-thick films)

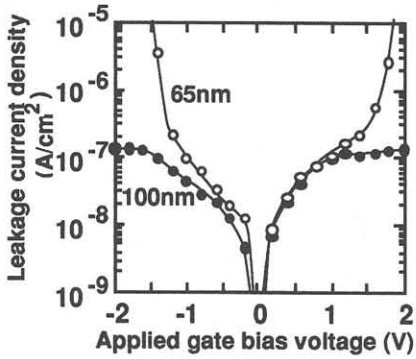

Fig. 8 I-V characteristics of 65nm- and 100nm-thick QE-PZT films.

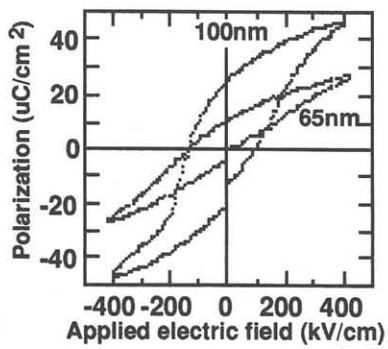

Fig. 9 D-E hysteresis loops of 65nm- and 100nm-thick QE-PZT films.

4. CONCLUSIONS

Quasi-epitaxial PZT growth on (111)Pt was performed by low temperature reactive sputtering and Rapid Thermal Annealing to improve electrical properties. PZT orientation was sensitive to Pt surface conditions and in-situ Ar-plasma cleaning was effective to remove disordered Pt surface. Optimum Pb-compositional ratio of QE-PZT films was around stoichiometric composition, where PZT films were grown as QE-growth. QE-PZT films had improved properties with so low leakage current and fatigue free in contrast to random oriented PZT films. QE-PZT films had smooth surface and annihilate columnar grain boundaries. Leakage current was kept as low as $2x10^{-7}A/cm^2$ at 1.5V-gate bias and equivalent SiO_2 thickness was kept around 0.4nm even on 65nm-thick QE-PZT films.

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