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Impact of low pressure consolidation annealing on electrical properties of sol–gel derived $Pb(Zr,Ti)O_3$ films

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Abstract

We demonstrate drastic improvement of electrical properties of sol–gel derived PZT thin films by using low-pressure consolidation annealing. PZT thin films have been prepared on $Pt/Ti/SiO_2/Si$ substrates using $Pb_{1.2}Zr_{0.4}Ti_{0.6}O_3$ source solution. We have employed low-pressure consolidation annealing at 400 °C for 10 min at 35 Torr before the crystallization anneal. The consolidated films were then annealed at 550–600 °C for 15–30 min in O_2 for crystallization. A remanent polarization (Pr) of 35 μC/cm^2 with a coercive filed (E_C) of 64 kV/cm was obtained for the PZT film crystallized at 600 °C with low-pressure consolidation process. Furthermore, it is also demonstrated that the leakage current density of the PZT film fabricated with low-pressure consolidation process is lower than that of the film fabricated by the conventional process. The possible crystallization mechanism of low-pressure consolidation process is discussed.

Keywords: Sol–gel process; Electrical properties; Ferroelectric properties; PZT; Ferroelectric random access memory (FeRAM)

1. Introduction

There is a growing need for high-speed, high-density, high-endurance, and low-power consumption nonvolatile memories for future computer and mobile applications. In particular, ferroelectric random access memory (FeRAM) has attracted much attention because the power consumption of FeRAM is much lower than those of other nonvolatile memories.[1,2] The standard memory cell structure of FeRAM consists of one MOSFET and one ferroelectric capacitor (1T1C-type), which is similar to that of dynamic random access memories (DRAMs). In 1T1C-type FeRAMs, the switching or non-switching current of ferroelectric capacitor is detected to read out the stored data by applying the voltage to the plate line, so this process is destructive readout. Based on this mechanism, we need a large remanent polarization (P_r) for ferroelectric materials used high-density FeRAM in the future, because when the ferroelectric capacitor sized is scaled down, the read out current becomes small. In addition, a small coercive field (E_C) is required for low-voltage operation and low power consumption. Among the various materials suitable for 1T1C-type FeRAMs, PZT has been most extensively studied and has already applied to practical FeRAMs. This is mainly because PZT has a large remanent polarization and relatively low crystallization temperature compared to the other candidates, such as $SrBi_2Ta_2O_9$ (SBT) and $(Bi,La)_4Ti_3O_{12}$ (BLT).

In this work, we have examined low-pressure consolidation process for sol–gel derived PZT thin films to improve the electrical properties. Similar technique was reported in sol–gel derived BLT thin films.[3,4]

2. Experimental procedure

We have prepared PZT thin films by the sol–gel technique with varying the consolidation pressure. The sample preparation procedure is as follows; First, 20% Pb-rich $Pb_{1.2}Zr_{0.4}Ti_{0.6}O_3$ (8 wt.%) source solution is spin-coated on $Pt/Ti/SiO_2/Si$ substrates at 3000 rpm for 20 s. The source solution used in this work is commercially available from Toshima MFG., Ltd., Japan and contains $Pb(C_8H_{16}O_2)_2$, $Zr(O\text{-}n\text{-}C_4H_9)_4$ and $Ti(O\text{-}n\text{-}C_4H_9)_4$ in 1-

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methoxy-2-propanol solvent. Then, the spin-coated films were dried in air at 240 °C for 5 min. We repeated this process for several times to obtain the desired thickness up to 140 nm. The thickness obtained by a single spin-coating was approximately 35 nm. After the drying process, films were consolidated at 400 °C for 10 min. The consolidation pressure was 15, 35 or 760 Torr. Next, crystallization annealing was conducted in O_2 atmosphere using a rapid thermal annealing (RTA) furnace. The RTA system used for consolidation and crystallization in this work has a horizontal quartz tube, infrared gold image furnace and a mechanical pump. The crystallization annealing condition is either at 550 °C for 30 min or at 600 °C for 15 min. The ramp rate for RTA annealing is 40 °C/s. After these processes, we deposited Pt top electrodes on the samples by electron-beam evaporation through a metal shadow mask for the electrical evaluation. Post-annealing was carried out at the same temperature as the crystallization annealing for 10 min in O_2 atmosphere.

The ferroelectric *P–E* (polarization versus electric field) hysteresis loops were measured using the RT66A ferroelectric test system (Radiant Technologies. Inc.) with a frequency of 120 Hz. Crystallographic property was characterized by X-ray diffraction (XRD) analysis. We evaluated surface morphology of the films by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Compositions of the films were measured by X-ray fluorescent analysis (XRF) and secondary ion mass spectrometry (SIMS).

3. Results and discussion

We first examined consolidation pressure dependence on the electrical properties of PZT thin films. Fig. 1 shows the obtained ferroelectric polarization–electric field (*P–E*) hysteresis loops of PZT films consolidated at various pressures. Dashed line, solid line, and dotted line show *P–E* hysteresis loops of the PZT films consolidated at 760, 35 and 15 Torr, respectively. All PZT films shown in Fig. 1 were crystallized at 550 °C for 30 min. It is demonstrated that electrical properties of the PZT film strongly depend on the consolidation pressure even if the samples are crystallized at the same temperature. When the PZT film is consolidated at 760 Torr, the obtained *P–E* hysteresis loop is slim and a remanent polarization (P_r) is as small as 10 μC/cm^2, which suggests the crystallization of the film is insufficient at 550 °C. When the consolidation pressure is reduced to 35 Torr, electrical properties of the PZT film is significantly improved as shown in Fig. 1. A square shape *P–E* hysteresis loop with a P_r of 28 μC/cm^2 was obtained for the PZT films crystallized at 550 °C when the films was consolidated at 35 Torr. If the consolidation pressure is further reduced to 15 Torr, degraded *P–E* hysteresis loop was observed. The remanent polarization decreases to around 10 μC/cm^2 for the PZT film consolidated at 15 Torr. It is demonstrated that the consolidation at 35 Torr results in best electrical properties, especially when the crystallization temperature is 550 °C.

Fig. 2 shows *P–E* hsyteresis loops of the PZT films crystallized at 600 °C for 15 min and consolidated at 760 Torr (dotted line) and 35 Torr (solid line). It is found from the comparison with Fig. 1 that increasing the crystallization temperature from 550 to 600 °C results in improvement of electrical properties of the PZT films even when the film was consolidated at 760 Torr. Excellent *P–E* hystereis loops were obtained for both films. This suggests the crystallization is pronounced at 600 °C regardless of the consolidation pressure. However, it is interesting to note that the remanent polarization (P_r) is increased from 27 to 35 μC/cm^2, while the coercive filed (E_C) is 64 kV/cm for both cases. We next plot the remanent polarization of the PZT films crystallized at 600 °C and consolidated at 35 and 760 Torr as a function of the applied voltage in Fig. 3 to show saturation properties of P_r. It can be seen in this figure, saturation properties is also improved for the PZT film consolidated at 35 Torr. The remanent polarization observed at 4 V of the PZT film fabricated with low-pressure consolidation is 94% of that observed at 8 V, whereas for the PZT film consolidated at 760 Torr, this value is 85%.

Fig. 4 shows leakage current density of the PZT films crystallized at 600 °C with and without low-pressure consol-

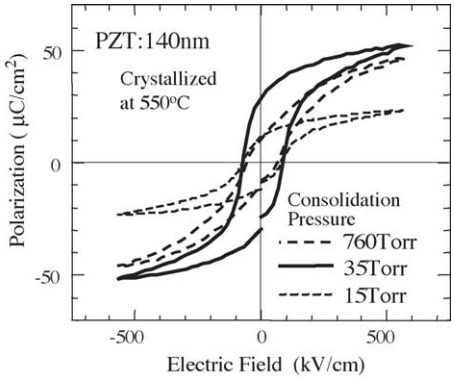

Fig. 1. Consolidation pressure dependence on *P–E* hsyteresis loop of the PZT films, crystallized at 550 °C.

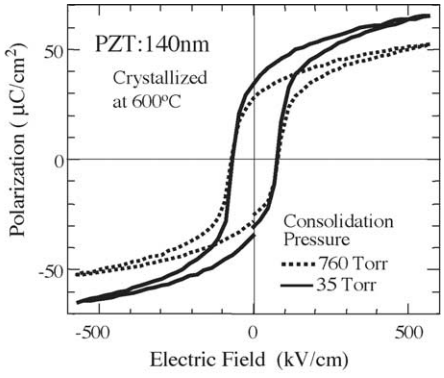

Fig. 2. *P–E* hysteresis loops of PZT films crystallized at 600 °C. Solid and dotted lines show *P–E* loops of the PZT consolidated at 35 and 760 Torr, respectively.

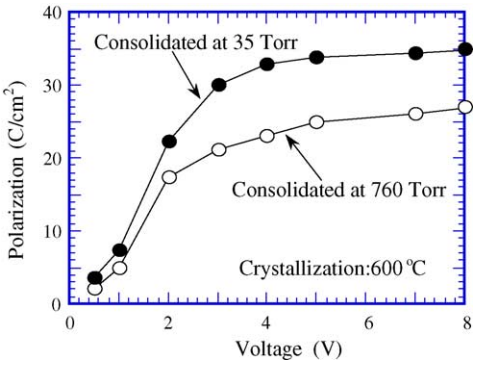

Fig. 3. Polarization of the PZT films with and without low-pressure consolidation process as a function of applied voltage. Both PZT films are 140 nm thick and crystallized at 600 °C.

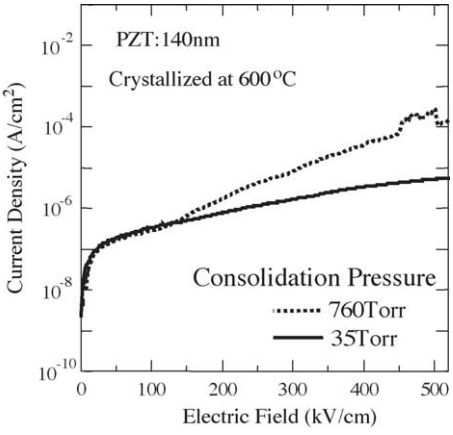

Fig. 4. Leakage current density of the PZT film crystallized at 600 °C after the consolidation at 35 Torr (solid line) and 760 Torr (dotted line).

idation process. It is found that relatively low leakage current densities are achieved for both PZT films and that the leakage current of the PZT film consolidated at 35 Torr is lower than that of the PZT film consolidated at 760 Torr especially when the applied electric field is large.

To clarify the effect of the low-pressure consolidation process, we measured composition of the PZT films by XRF and SIMS. Table 1 listed Pb, Zr, and Ti compositions in the PZT films fabricated with and without low-pressure consolidation process and crystallized at 600 °C, measured by XRF. It is found that the Zr and Ti compositions in the PZT film agree with the compositions of source solution, regardless of the consolidation pressure. On the other hand, Pb composition

Table 1
Pb, Zr and Ti compositions in the PZT films after 600 °C crystallization, measured by XRF

	PZT consolidated at 760 Torr	PZT consolidated at 35 Torr
Pb	1.19	1.14
Zr	0.4	0.4
Ti	0.59	0.58

The composition of Pb, Zr and Ti in the source solution is 1.2, 0.4 and 0.6, respectively.

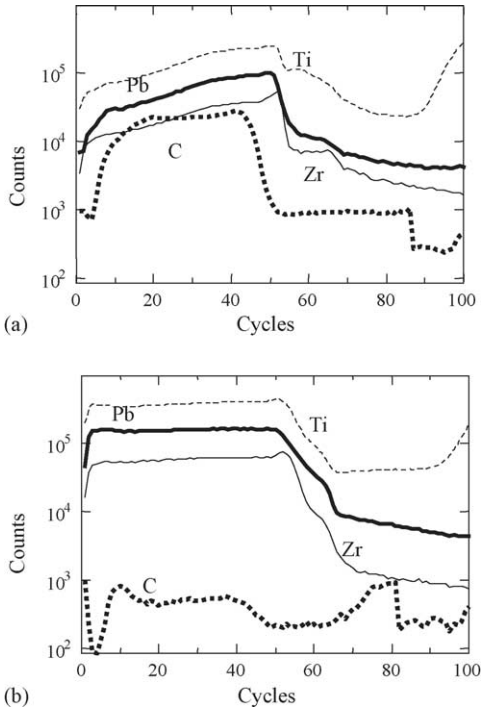

Fig. 5. Depth profiles of Pb, Zr, Ti and C concentrations in the consolidated PZT film before the crystallization. Consolidation pressure is (a) 760 Torr and (b) 35 Torr.

of the PZT film consolidated at 35 Torr is 1.14, whereas that of the film consolidated at 760 Torr is 1.19 which agrees the Pb composition of the source solution. The Pb composition in the film consolidated at 35 Torr is slightly decreased probably because of the re-evaporation of Pb. To investigate composition change by low-pressure consolidation process more precisely, depth profile of Pb, Zr, Ti, and C concentrations were measured by SIMS. Fig. 5 shows depth profile of Pb, Zr, Ti and C of the PZT films consolidated at (a) 760 and (b) 35 Torr. The measurements were carried out just after the consolidation before the crystallization. No significant composition change is observed for Zr, Ti, and Pb. Comparing depth profile of Pb with that of Zr and Ti, we did not observe significant composition change even for Pb for the PZT film at this stage. On the other hand, it is found that drastic decrease of carbon concentration can be achieved by consolidating the film at 35 Torr. Fig. 6 shows depth profile of Pb, Zr, Ti and C of the PZT films after crystallization anneal. The samples are PZT films consolidated at (a) 760 and (b) 35 Torr and both PZT films were crystallized at 600 °C for 15 min. It is interesting to note that the Pb composition profile has a gradient in the PZT film consolidated at 35 Torr, whereas it is constant in the PZT film consolidated at 760 Torr. The average composition of Pb is therefore, lower for the PZT film consolidated at 35 Torr than that of PZT film consolidated at 760 Torr. Since the Pb concentration at the surface is higher than that at the substrate interface, it is considered that the re-evaporation of Pb is enhanced during the crystallization anneal for the PZT film which was consolidated at low pressure. On the other

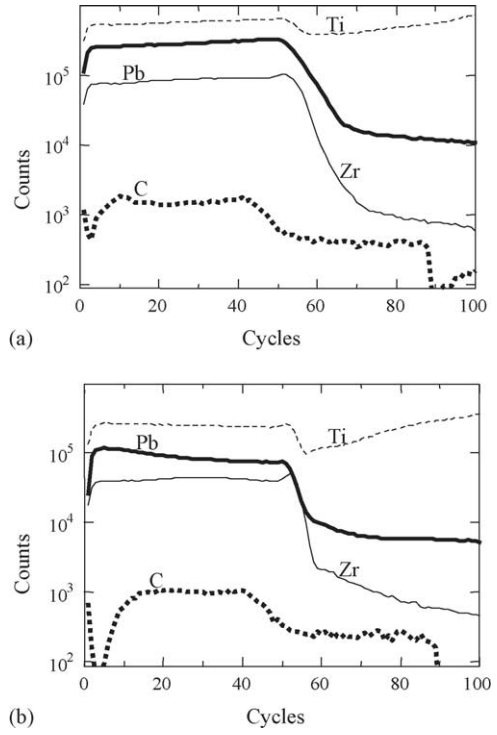

Fig. 6. Depth profiles of Pb, Zr, Ti and C concentrations in the PZT film after the crystallization at 600 °C for 15 min (a) consolidated at 760 Torr and (b) consolidated at 35 Torr.

hand, carbon concentration is comparable for the PZT films after the crystallization.

We have also fabricated PZT films using $Pb_{1.1}Zr_{0.4}Ti_{0.6}O_3$ which contains 10% excess Pb and stoichiometric $Pb_{1.0}Zr_{0.4}Ti_{0.6}O_3$ source solutions. In the case of $Pb_{1.1}Zr_{0.4}Ti_{0.6}O_3$, we have observed similar improvements by the low-pressure consolidation process. When the film was consolidated at atmospheric pressure after spin-coating and drying, the crystallized PZT film was leaky and the *P–E* hysteresis could not be measured, whereas excellent *P–E* hysteresis loops were obtained by the low pressure consolidation process at 35 or 15 Torr. We have obtained a remanent polarization (P_r) of as large as 32 μC/cm^2 for the PZT film which was consolidated at 400 °C at 35 Torr and crystallized at 600 °C using $Pb_{1.1}Zr_{0.4}Ti_{0.6}O_3$ source solution. On the other hand, good electrical properties could not be obtained for the PZT films if the stoichiometric source solution was used. Hence, excess Pb in the source solution is necessary to obtain good electrical properties.

From these observations, we briefly discuss the crystallization mechanism of PZT films with low pressure consolidation process as follows: First, the low-pressure consolidation effectively removes the organic substances during the consolidation process. Hence, the amorphous or microcrystalline precursor film with low residual carbon concentration is obtained by low-pressure consolidation. Secondly, outdiffusion of excess Pb may be enhanced in this low-carbon-content precursor film, which promotes the formation of crystalline nuclei. Consequently, dense film can be obtained by the low-pressure consolidation process and Pb composition of the PZT film is slightly reduced for the PZT film fabricated with low-pressure consolidation. Indeed, SEM observation revealed that the PZT film crystallized at 600 °C by conventional process has rough surface and large grain size about 1.5 μm in diameter, whereas the PZT film consolidated at 35 Torr has smooth surface and its grain size is around 150 nm in diameter in spite of the same crystallization temperature of 600 °C. These observations suggest that the formation of the crystalline nuclei is enhanced by the low-pressure consolidation and that the nuclei concentration in the film after low-pressure consolidation is much higher than that in the film after atmospheric-pressure consolidation. This will result in the small crystalline grains and dense PZT films, which also realize good ferroelectric properties and low leakage current.

4. Summary

We have demonstrated that the electrical properties of sol–gel derived PZT thin films, such as remanent polarization and leakage current, can be improved by using low-pressure consolidation annealing. A remanent polarization (P_r) as large as 35 μC/cm^2 with a coercive filed (E_C) of 64 kV/cm has been obtained for the PZT film crystallized at 600 °C after the consolidation of 35 Torr. In addition, the leakage current density of the PZT film consolidated at 35 Torr is lower than that of the film consolidated at 760 Torr. It has been also demonstrated that the residual carbon concentration in the consolidated film is drastically decreased by the low-pressure consolidation process. This may promote the Pb out-diffusion and crystalline nuclei formation in the film, which will results in good electrical properties, smooth surface and small grain size in the sol–gel derived PZT films.

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