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Effects of the deposition and patterning processes of the top electrode on the ferroelectric properties of Pt/Pb(Zr,Ti)O_3/Pt thin film capacitors

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Abstract The deformation in the hysteresis loop of Pt/PZT/Pt thin film capacitors due to deposition and patterning processes of the top electrode has been investigated. The PZT film was aged during the deposition of the top electrode and was positively poled during reactive ion etching (RIE) of the top electrode. The PZT film having sputtered top electrode was very sensitive to the RIE process. The film with a thinner top electrode showed less initial switching polarization due to less compressive stress, but better fatigue characteristics due to an enhanced partial switching region.

Introduction

Ferroelectric lead zirconate titanate (PZT) thin films have been investigated for use in nonvolatile memory devices, integrated capacitors on Si, and many sensors [1, 2]. Patterning of PZT and Pt electrode materials is one of the key process issues in the integration of these films into silicon devices because they do not easily react with etching gases and do not form volatile species at low temperatures [3, 4]. Unfortunately, the ferroelectric film is exposed to high energy photon radiation and energetic ion bombardment during sputtering and RIE of the top electrode for fabrication of integrated ferroelectric capacitors. The radiation and bombardment of the PZT film surface may be enough to modify the ferroelectric film and, thus, deform the hysteresis loop [5].

The deformation in the hysteresis loop of the PZT film caused by thermally and optically induced defects has been investigated [6, 7]. However, few studies have been devoted to understanding the change in the hysteresis loop during preparing of the top electrode of a Pt/PZT/Pt capacitor systematically. In this paper, we present the influence of the top electrode deposition and patterning methods on the ferroelectric properties of $PbZr_{0.2}Ti_{0.8}O_3$ film. The top electrode thickness dependence of the reliability is also discussed.

Experimental

The PZT films, 200 nm thick, were prepared by using a sol–gel method on a substrate of Pt/Ti/SiO_2/Si layers. The precursor materials used were lead acetate-3-hydrate, zirconium propoxide, and titanium isopropoxide. The precursors were synthesized by distilling and refluxing in butoxy-ethanol. The amount of excess lead was 16% and the Zr/Ti (20/80) composition was selected because the deformation in its hysteresis loop was very sensitive to the process conditions. The thicknesses of Pt and Ti were 100 and 10 nm, respectively. Sequential spin coating and drying steps were followed by a crystallization for 30 min at 600 °C in air.

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Prior to spin coating the PZT film, the Pt electrode was annealed at 700 °C for 10 min.

A Pt top electrode was deposited by dc magnetron sputtering without heating the substrate or deposited by pulsed laser deposition (PLD). The third harmonic of a Nd:YAG laser (355 nm, 10 Hz, 2.5 J/cm^2) was used for the PLD. Ablation was carried out in an Ar atmosphere of 300 mTorr with a target to substrate distance of 7 cm without heating the substrate. The Pt top electrode was patterned by shadow mask or RIE using Ar gas for 50 min with a photoresist as a mask. Plasma ashing was done using SF_6/O_2 gas for 5 min for removing the photoresist.

The structure of the PZT film was assessed using X-ray diffraction (XRD). All the PZT films were entirely in the perovskite phase with no detectable pyrochlore or amorphous scattering and had preferential (111) orientation. Sequential processes, such as Pt-sputtering, RIE, and annealing, did not change the XRD pattern. The polarization–electric field (P–E) hysteresis loop was measured using a modified Sawyer-Tower circuit with HP54503A digitizing oscilloscope. We applied 1 kHz sinusoidal voltage signals with amplitudes varying from 1 to 10 V on the top electrode. To measure pulse switching polarization, two positive and two negative pulses with 150 ns width were applied using HP8116A pulse/function generators. Consecutive pulses of the same polarity and of the opposite polarity were used to measure the nonswitched polarization (Q_{ns}) and the switched polarization (Q_s), respectively. Endurance cycling of the capacitors was done at a frequency of 2 MHz. Both positive and negative pulses of 125 ns widths were applied at 125 ns intervals.

Results and discussion

Figure 1 shows the P–E hysteresis loop of PZT films for different top electrode preparation methods. Constricted hysteresis loops were observed as shown in Fig. 1(a) in the capacitor with the sputtered top electrode patterned by shadow mask. A decrease in the coercive field was also observed after high energy photon radiation of triglycine sulfate and $BaTiO_3$ single crystals [8]. The physical origin of the constriction is not clear at this time. However, the constriction phenomenon seems to be related to space charges formed by high energy photon radiation during sputtering of Pt. Space charges such as reduced Ti ion and oxygen vacancy formed by the radiation can be located in the interface between the electrode and the ferroelectric thin film. A reduced Ti ion can be associated with an oxygen vacancy, resulting in a defect dipole. The dipole can orient parallel to the spontaneously polarized lattice. On application of a bias, the polarization switched, however,

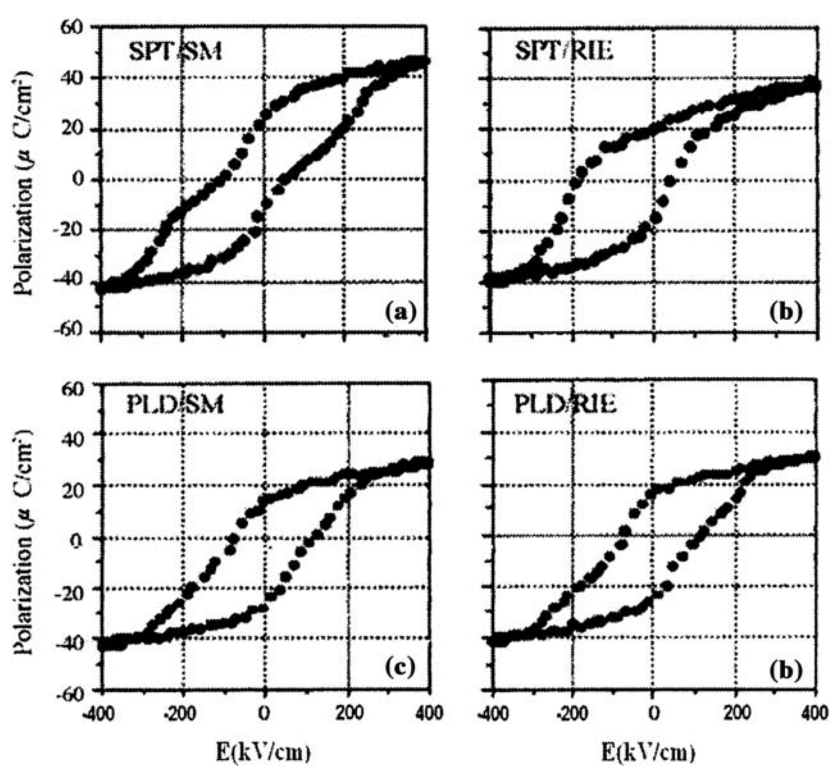

Fig. 1 Hysteris loops of PZT (20/80) films for different top electrode preparation methods

the defect configuration remained unchanged. The ferroelectric film was aged during sputtering of top electrode, resulting in a constricted loop.

A large shift of the hysteresis loop along the electrical field axis was observed as shown in Fig. 1(b) in the film with the top electrode deposited by sputtering and patterned by RIE. The loop has shifted toward the negative side, which indicates the existence of an internal field (E_{in}) that points to bottom electrode. It is reported that the internal field is related to associated defect pairs consisting of negatively charged acceptor ions and positively charged oxygen vacancies ($V_O^{\cdot\cdot}$), forming electric dipoles [9, 10]. It is believed that associated defect pairs are aligned parallel to the polarization by the dc plasma potential generated during RIE of Pt.

The hysteresis loop for the film with the top electrode formed by PLD with a shadow mask is shown in Fig. 1(c). Compared to the film of Fig. 1(a), the sputtering process was found to generate much more space charges than the PLD process. The hysteresis loop for the film formed by PLD and RIE, Fig. 1(d) shows slanted and constricted a little. It can be said that the film having sputtering process is seriously deformed during the RIE process.

PZT capacitors with Pt top electrode formed by sputtering and patterned by RIE, Fig. 1(b), were annealed for 10 min in air to examine the effect of

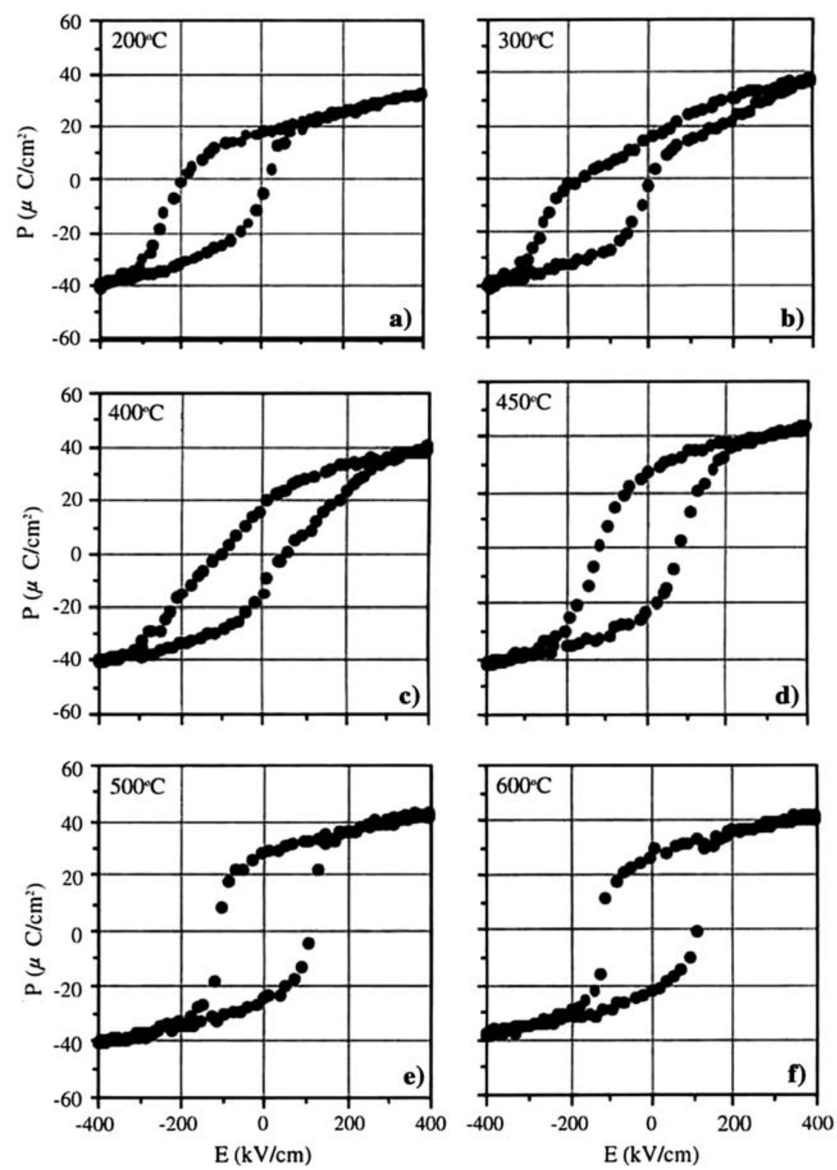

Fig. 2 Hystersis loops of PZT (20/80) films with different post-RIE annealing temperatures

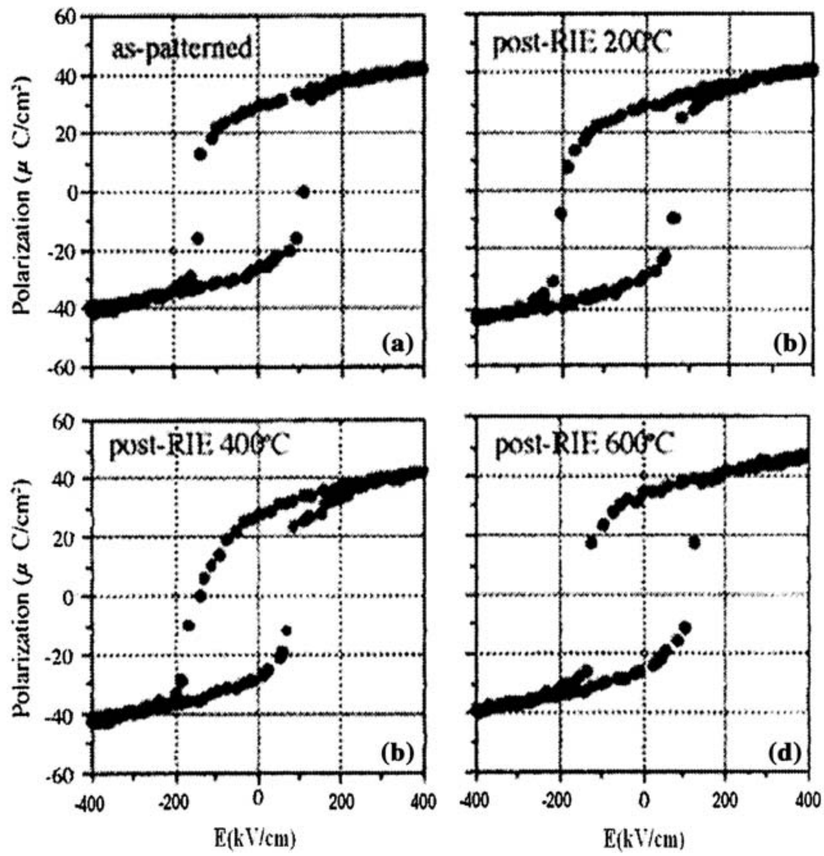

Fig. 3 Hysteresis loops of PZT (20/80) films with pre-RIE annealing at 600 °C for 10 min as a function of the post-RIE annealing temperature

post-RIE annealing. Figure 2 shows P–E loops of PZT films for different post-RIE annealing temperatures. The internal field shows its maximum value for the film annealed at 200 °C and decreases with further increases in the annealing temperature. Some parts of the loops are observed to shift from the left to the right with increasing annealing temperature from 200 to 400 °C. This result strongly suggests that the field shift and the slant are caused by space charges trapped in interfaces between the electrode and the ferroelectric thin film rather than in the nonferroelectric passive layer. When a poled ferroelectric film remains at 200 °C, charge trapping accelerates at both ends the interfaces, and migration of charges occurs at higher temperature. A uniform distribution of trapped charges would not contribute much to the field shift. The hysteresis loop of the capacitor annealed at 400 °C shows a constriction in the middle of the loop and is quite similar to that of the capacitor with the top electrode formed by sputtering with a shadow mask, Fig. 1(a).

The film annealed at 450 °C, near the Curie temperature of the 20/80 PZT film, exhibits a slanted loop without any constriction in the middle of the loop. It can be said that defect related to the constriction is not caused by a crystal structure defect such as a second phase. The films annealed above 500 °C have no internal fields and have well saturated loops.

In order to separate the effect of RIE from that of sputtering, some samples were annealed at 600 °C for 10 min before RIE of the Pt. Figure 3 shows P–E loops of 600 °C pre-RIE annealed films with different post-RIE annealing temperatures. A small internal field was observed in the as-patterned film. The internal field has its maximum value in the film annealed at 200 °C. A ferroelectric film seems to be poled during RIE. When the film remains at 200 °C, charge trapping accelerates at both ends the interfaces. The internal field calculated by using $(|E_c^-| - E_c^+)/2$ is about 60 kV/cm, so the voltage shift is evaluated to be 1.2 V for the 200 nm thick film. In addition to the field shift, the deformation of the hysteresis loop along the polarization axis is observed in the film annealed at 400 °C. An asymmetry of the polarization and the constriction in the loop were also observed during post-RIE annealing, particularly for the low Zr/Ti PZT film [11]. A possible explanation for the small positive polarization is probably due to the combined effects of both the constriction in the loop and the internal field. The film annealed at 600 °C after RIE shows a well-saturated loop.

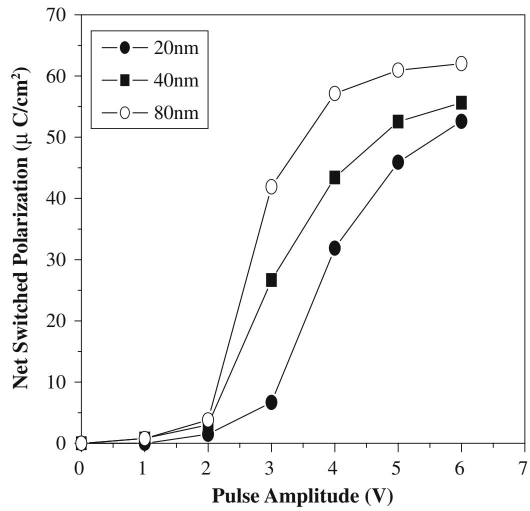

Fig. 4 Switching characteristics of PZT (20/80) films as a function of the thickness of the top electrode

Top electrode annealing can change the stress in Pt, which in turn can affect the properties of PZT film. In order to examine the effect of thermal stress due to the top electrode annealing on PZT film, the top electrode thickness dependence of the switching properties was measured after annealing Pt/PZT/Pt capacitors at 600 °C in air. All films exhibited well-saturated hysteresis loops, regardless of the top electrode thickness. The difference between the switched (Q_s) and the nonswitched polarization (Q_{ns}) is net switched polarization ($2P_r$) and is the most interesting parameter in ferroelectric memories. Figure 4 shows that net switched polarization values of PZT films as a function of the top electrode thickness. There is a dependence of switching charges on the top electrode thickness. The net switched polarization increases with the top electrode thickness. The films have preferential (111) orientation, however, a (100) domain reorientation can take place to accommodate the compressive stress induced by the top electrode during the high temperature annealing and the cooling of the capacitor. Therefore, *c*-axis nuclei are likely to grow at the expense of the *a*-axis domain. Spierings et al. [12] also observed the stress effect of the top electrode on Pt/PZT/Pt capacitors with composition near morphotropic phase boundary, which agrees with our result.

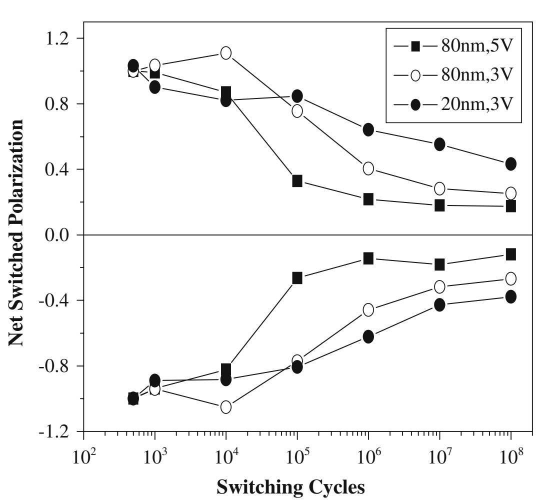

Fig. 5 Fatigue characteristics of PZT (20/80) films with different top electrode thicknesses and pulse amplitudes

The normalized net switching polarizations as a function of the number of switching cycles are shown in Fig. 5. The fatigue rate can be retarded considerably by decreasing the pulse amplitude and/or the top electrode thickness. The PZT film with a thinner top electrode exhibits less initial polarization, but better endurance characteristics. It is well known that the fatigue improves by lowering the pulse amplitude. It should be noted that the improvement of fatigue rate for the film with a thinner electrode is related to a reduction in the switching polarization due to less mechanical poling.

Conclusions

Ferroelectric thin film capacitors were positively poled by a dc plasma potential during RIE of Pt. The hysteresis loops of the capacitors were found to be shifted, slanted, and constricted by space charges trapped at the interface between the electrode and ferroelectric thin films. The PZT film having sputtering damage was very sensitive to RIE damage. The top electrode thickness dependence of the switching polarization can be explained by thermal stress induced by annealing of Pt/PZT/Pt capacitor. The PZT film with a thinner top electrode exhibited better fatigue characteristics due to an enhancement of the partial switching region.

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