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Crystallinity of $Pb(Nb_{0.04}Zr_{0.28}Ti_{0.68})O_3$ capacitors on ferroelectric properties

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Abstract Polycrystalline and epitaxial heterostructure films of $La_{0.5}Sr_{0.5}CoO_3/Pb(Nb_{0.04}Zr_{0.28}Ti_{0.68})O_3/La_{0.5}Sr_{0.5}CoO_3$ (LSCO/PNZT/LSCO) capacitors were evaluated in terms of low voltage and high speed operation in high density memory, using TiN/Pt conducting barrier combination. Structural studies for a high density ferroelectric memory process flow, which requires the integration of conducting barrier layers to connect the drain of the pass-gate transistor to the bottom electrode of the ferroelectric stack, indicate complete phase purity (i.e. fully perovskite) in both epitaxial and polycrystalline materials. The polycrystalline capacitors show lower remnant polarization and coercive voltages. However, the retention, and high-speed characteristics are similar, indicating minimal influence of crystalline quality on the ferroelectric properties.

Key words Ferroelectric, Epitaxial, Polycrystalline, PNZT, Grain boundary

1. Introduction

Epitaxial ferroelectric films have several advantages over polycrystalline films in the areas of basic scientific research and actual applications. The primary advantage of epitaxial over polycrystalline films is in the interpretation of ferroelectric properties. High angle grain boundaries and complex interfaces between randomly oriented crystallites in the ferroelectric (FE) capacitor and the electrodes complicate the interpretation of polycrystalline films. For example, epitaxial FE capacitors can be assumed to have simpler 90° or 180° ferroelectric domains [1]. With this simplification, the main factors affecting FE properties are; 1) lattice mismatch between the ferroelectric and the electrodes, 2) self-strain during phase transformation, and 3) thermal expansion mismatch during cooling [2].

A high density Ferroelectric Random Access Memory (FRAM) process requires the integration of conducting barrier layers to connect the drain of the pass-gate transistor to the bottom electrode of the FE stack. Conventionally, this is accomplished through a highly doped poly-Si plug. An alternative approach is to use an epitaxial conducting Si-plug [3] that will enable the growth of epitaxial ferroelectric capacitors. Epitaxial or oriented FE films ($Pb(Zr, Ti)O_3$ (PZT) type) have been reported using different buffer layers on various substrates. For instance, oriented $LSCO/(Pb_{0.9}La_{0.1})(Zr_{0.2}Ti_{0.8})O_3$ (PLZT)/LSCO heterostructures were grown on (001) $Pt/SiO_2/Si$ using a bismuth titanate template layer by pulsed laser deposition (PLD) [4]. Epitaxial PZT films were grown on Si (100) using $SrTiO_3/TiN$ buffer layer by PLD [5]. In this article, the epitaxial growth of LSCO/PNZT/LSCO films on Si (100) at 600°C using epitaxial Pt/TiN conducting barriers by PLD is reported. Electrical properties (ferroelectric hysteresis, retention, and high-speed polarization) for nonvolitile memory application were measured and compared to those of polycrystalline LSCO/PNZT/LSCO films on poly-Si/Si (100).

2. Experimental Details

Epitaxial thin film heterostructures, (LSCO/PNZT/LSCO/Pt/TiN), were grown on hydrogen terminated (100) Si by in-situ pulsed laser deposition (PLD) at 600°C. An oxygen ambient of 100 mTorr was used during deposition and the heterostructures were cooled in 1 atm of oxygen after deposition. Test capacitors, 50 μm in diameter, were fabricated using photolithography and a subsequent lift-off process. The top LSCO between the test capacitors was etched using nitric acid; Pt acted as a mask to provide electrical isolation. Contact to the bottom electrode was made directly through a large Pt pad. The thickness of Pt layers was 2,000 Å, which provided underlying TiN (500 Å) layers with good enough oxidation prevention during FE capacitor deposition (600°C and oxygen ambient). Additionally, epitaxial Pt/TiN combination films are likely to have better resistance to oxygen diffusion and, therefore, oxidation resistance at high

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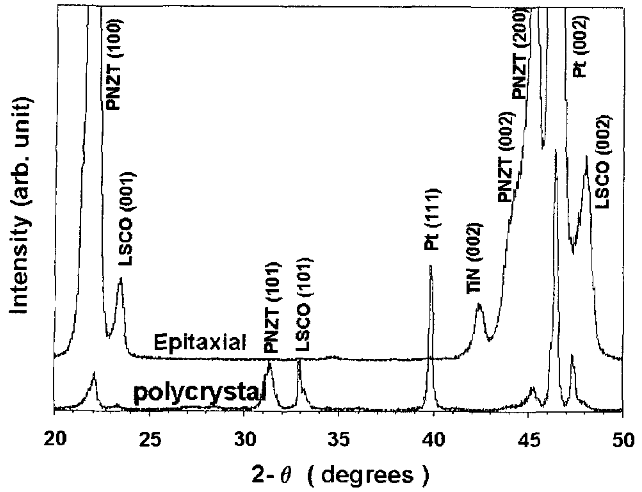

Fig. 1. X-ray diffraction θ-2θ scan for epitaxial and polycrystalline LSCO/PNZT/LSCO capacitor heterostructures using Pt/TiN conducting diffusion barrier grown on (100) Si and poly-Si/Si (100), respectively.

temperature compared to polycrystalline films.

3. Results and Discussion

The θ-2θ x-ray scans of both polycrystalline and epitaxial films are compared in Fig. 1. θ-2θ X-ray scans (Siemens D5000) revealed a strong (00*l*) orientation for the epitaxial whole stack while phi-scans of the epitaxial individual layers show in-plane orientation locked with the substrate. This result suggests that the PNZT layer is free of large angle grain boundaries. The θ-2θ x-ray scans of epitaxial films reveal a splitting of the (002) PNZT peak, indicating that the PNZT layer consists of a mixture of c-axis and a-axis domains oriented normal to the substrate. This situation has also been observed in PLZT on $LaAlO_3$ substrates earlier [6]. It is speculated that this is caused by the stresses generated during cooling as a result of the difference in thermal expansion of the LSCO/PNZT/LSCO layers and Pt/TiN on Si [7]. Polycrystalline films also have highly (00*l*) orientation.

Cross-section transmission electron microscopy studies (Philips CM20T) for epitaxial layers, shown in Fig. 2(a), revealed several important aspects: First, there was no evidence of any reaction or oxidation on products at the Pt (200 nm)/TiN (60 nm) interface, indicating that the epitaxial Pt layer acted as a good barrier to oxygen diffusion. Second, the interfaces in the LSCO (80 nm)/PNZT (200 nm)/LSCO (80 nm) layers are also free of reaction products. Fig. 2(b) shows a representative TEM picture of polycrystalline FE capacitor layers grown at 550°C. The polycrystalline films showed no interfacial reaction. However, the LSCO/PNZT/LSCO stack showed columnar grains with about 500 Å width.

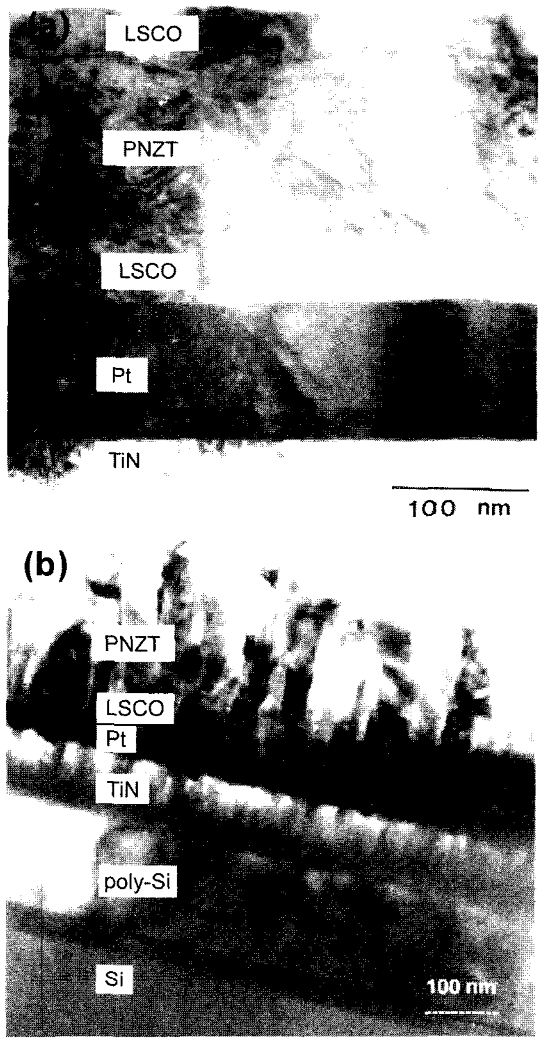

Fig. 2. Bright field TEM image of (a) epitaxial LSCO/PNZT/LSCO/Pt/TiN heterostructure on Si (100 and (b) polycrystalline LSCO/PNZT/LSCO/Pt/TiN heterostructure on poly-Si/Si (100).

Electrical measurements were made using a pulsed testing system (Radiant Technologies, RT66A) and a high speed test set-up. Ferroelectric hysteresis loops, shown in Fig. 3(a), were obtained for epitaxial and polycrystalline (top and bottom contacts). Pulsed polarization measurements show that ΔP (ΔP = P* − P^; P*: switched polarization, P^: non-switched polarization.) of epitaxial and polycrystalline films is larger than 20 and 10 $\mu C/cm^2$ for applied voltages of 2 V and pulse width of 2 msec with a coercive field of about 48 and 35 kV/cm, respectively, as shown in Fig. 3(b). Such high values of ΔP in epitaxial films are sufficient for low power (1.5 V~3 V), nonvolatile storage. Polarization ΔP and coercive voltage Vc through top and bottom contacts in

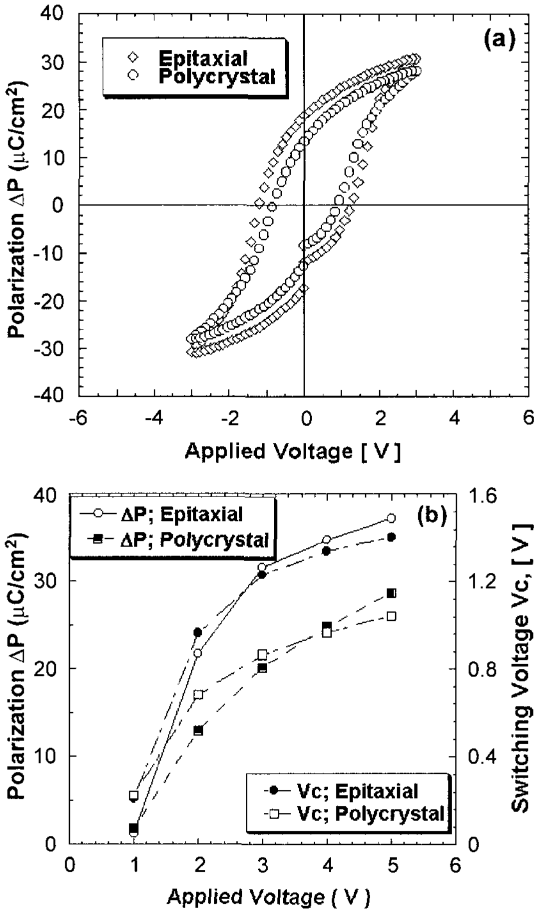

Fig. 3. (a) Hysteresis loops for epitaxial and polycrystalline capacitors, measured at applied voltage of 3 V for epitaxial and polycrystalline LSCO/PNZT/LSCO capacitor. (b) Pulsed polarization (P*, switched – P^, nonswitched) and coercive voltage as a function of applied voltage.

the polycrystalline films showed minimal differences.

One of important reliability issues in FERAM is retention property. Capacitors need to be maintained in a logic state (i.e., a polarization state) for a long time (retention time), and FERAM devices should clearly discriminate between two-logic states (i.e., a logic 1 and 0 state), irrespective of the retention time. To study the memory state discrimination capability (the logic "1" and "0" states), retention tests were performed with a write voltage of –3 V (2 ms pulse width) followed by a read at +2.5 V (2 ms pulse width). Delay between the write and read pulses is the retention time. Polarization ΔP of epitaxial capacitor is about 10 μC/cm^2 at the retention time of 10^5 second. Extrapolation from this curve indicates that the ΔP value of epitaxial film decreases less than 2 μC/cm^2 within about five years, as shown in Fig. 4(a). The reading failure in FE memory occurs if the ΔP value is less than 2 μC/cm^2.

Consequently, the requirements for high performance FERAM, that is, larger than 10 years retention time at the pulse width of less than 1 μsec (high speed), cannot be satisfied. Retention failure in polycrystalline films will be faster than in epitaxial films. The loss of polarization during a retention time is attributable to backswitching processes of stored polarization. These processes occurring without an external field are driven primarily by internal depolarizing field. The retention loss can be fitted by a stretched exponential, that is, equation of the form $y = 1 - \exp(-kt^n)$. In various systems, a stretched exponential behavior with $n < 1$ has been characterized as a dispersive transport or random walk type process [8-9]. In retention tests, retained polarization (ΔP) after retention loss is typically measured, and this value corresponds to $1 - y$ in the above relation. Plots of ln (ΔP_n) as a function of retention time was well-fitted by the stretched exponential, as shown in Fig. 4(b), where $\Delta P_n = (\Delta P_t/\Delta P_i)$, and ΔP_t and ΔP_i are remaining polarization at each retention time and initial polar-

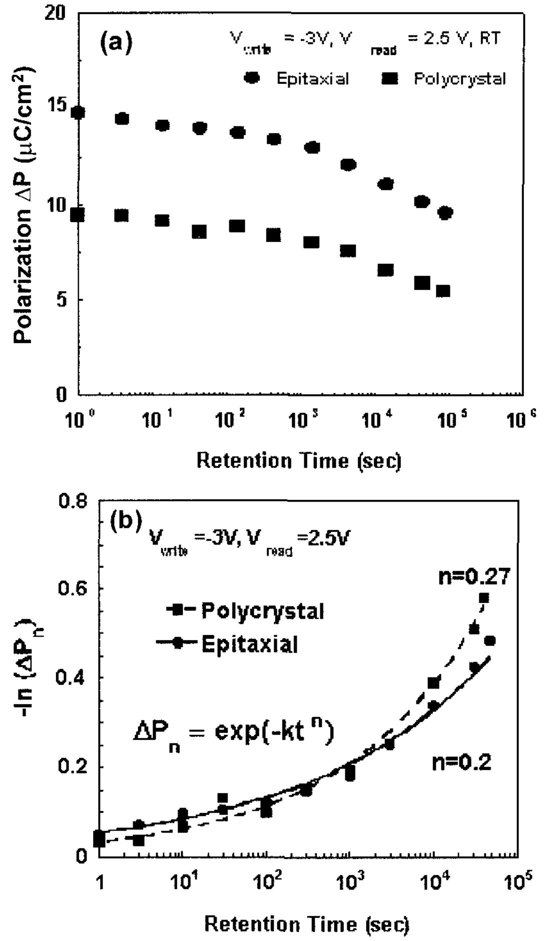

Fig. 4. (a) Logic state retention data (ΔP = P* – P^) for epitaxial and polycrystalline capacitors using Pt/TiN on Si wafers. (b) Natural logarithm of normalized ΔP as a function of retention time.

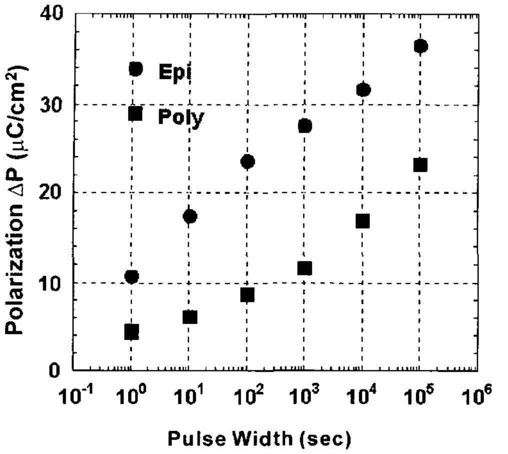

Fig. 5. Pulse width dependence of polarization for epitaxial and polycrystalline heterostructures (LSCO/PNZT/LSCO) at 3 V.

ization, respectively. Measured n value of epitaxial and polycrystalline capacitor was 0.2 and 0.27, respectively. Epitaxial films showed lower back-switched polarization during the retention tests. These results suggest that the backswitching process occurs by a random walk process. The polarization values (ΔP) were measured through the high-speed set-up, simulating a real memory circuit as a function of pulse width down to 1 μsec. The polarization of epitaxial FE capacitor decreases with shorter pulse width, shown in Fig. 5. ΔP value of epitaxial FE capacitors at 1 μsec pulse width, corresponding to a speed rate of 1 MHz is about 10 $\mu C/cm^2$. This ΔP value is not sufficient for high-speed performance larger than 10~100 MHz. The polarization of polycrystalline capacitor also shows almost the same behavior as epitaxial film, and ΔP at 1 μsec pulse width is about 5 $\mu C/cm^2$, smaller than that of epitaxial films.

4. Summary

Epitaxial and polycrystalline growth of LSCO/PNZT/LSCO on Si, using a Pt/TiN conducting barrier layer by pulsed laser deposition, was demonstrated. The polycrystalline capacitors show lower remanent polarization and coercive voltages, compared with epitaxial capacitors. A stretched exponential fitting for retention loss indicates that the back-switching process involved in retention loss occurs by a random walk type process. These results correlate to a lower decay of retained polarization in epitaxial capacitor. Pulse width dependence measurement of ΔP polarization showed that PNZT capacitors have insufficient ΔP for a high speed operation (larger than 10 MHz). This heterostructure shows excellent resistance to bipolar fatigue and retention behavior. This whole stack is compatible with current Si technology and could accelerate the realization of commercially viable high density memory devices for operation at low voltages.

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