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La doping into $Pb(Zr, Ti)O_3$ capacitors on domain structures

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Abstract The ferroelectric domain variation and electrical performance of $Pb(Zr,Ti)O_3$ (PZT) based capacitors through La additions were systematically studied. La substitution up to 10 % was performed to lower the coercive and saturation voltages of epitaxial ferroelectric capacitors grown on Si using a $(Ti_{0.9}Al_{0.1})N/Pt$ conducting barrier composite. Ferroelectric capacitors substituted with 10 % La show significantly lower coercive voltage compared to capacitors with 0 % and 3 % La. This is attributed to a systematic microstructure change into 180° domain and decrease in the tetragonality (i.e., c/a ratio) of the ferroelectric phase. These capacitors show promise as storage elements in low power memory architectures.

Key words Ferroelectric, Domain, PZT, La, Doping, Low voltage

1. Introduction

There is currently considerable research and development effort aimed at developing nonvolatile ferroelectric memories using the intrinsic remnant polarization available in ferroelectric materials. One specific issue is the operability of the ferroelectric capacitors at voltage levels lower than the standard 5 V operation. Low voltage operation is particularly desirable in future generation memory devices, which will function in information systems such as wireless communications. Reduction in the operating voltage level means that the ferroelectric capacitor materials properties also have to be optimized further. Particularly, it is desirable that the hysteresis loops saturate at applied voltages of the order of 1.5~3 V with coercive voltage in the range of 0.5~0.7 V.

However, the correlation between capacitor microstructure, especially ferroelectric domains, and electrical properties has not been investigated completely. 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 capacitor and the electrodes complicate the interpretation of polycrystalline films. For example, epitaxial ferroelectric capacitors can be assumed to have simpler 90° or 180° ferroelectric domains [1]. With this simplification, the main factors affecting ferroelectric properties are first lattice mismatch between the ferroelectric films and the electrodes, secondly self-strain during phase transformation, and finally thermal expansion mismatch during cooling [2]. Thus, epitaxial ferroelectric films were used to simplify the microstructure relevance. In this paper, results of experiments aimed at addressing the correlation issue between ferroelectric domain structures and low voltage operation, using La substituted PZT (PLZT) up to 10 % as ferroelectric thin layers with La-Sr-Co-O (LSCO) electrodes are reported.

2. Experimental Details

Heteroepitaxial PLZT/LSCO thin films were grown by pulsed laser deposition (PLD), with a $(Ti_{0.9}Al_{0.1})N/Pt$ conducting barrier layer composite directly on (100) Si, an integration scheme that is crucial for a high density memory architecture. Epitaxial $(Ti_{0.9}Al_{0.1})N$ films of 600 Å thickness were deposited on hydrogen-terminated (100) Si using a target of the same nominal composition. $(Ti_{1-x}Al_x)N$ barriers have recently attracted attention due to their better oxidation resistance and stability at elevated temperature. The PLZT layer thickness was 1500 Å and the top and bottom LSCO layers were each 700 Å. Transmission electron microscopy studies were carried out on a JEOL 4000FX microscope operated at a voltage of 300 kV. Electrical measurements were carried out using a Radiant technologies RT66A tester.

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3. Results and Discussion

The crystalline quality and phase purity of the ferroelectric stack in both wafers was confirmed to be pure perovskite with a high degree of [100] orientation by x-ray diffraction studies shown in Fig. 1(a). Furthermore, x-ray phi-scans revealed a strong degree of in-plane orientation in all the layers, similar to what it was already reported for epitaxial PNZT thin films on similar substrates [3]. One systematic change with La substitution is the c-axis lattice parameter and the c/a ratio. As the La content into PZT (the ratio of Zr/Ti is 20/80) capacitors increases, the c-axis parameter of bulk decreases, but the a-axis parameter of bulk increases. Comparing films to bulk, c-axis parameter of films is slightly smaller, but a-axis parameter is larger, and the difference of a-axis parameter is in the range of 0.05~0.1 Å. These a-axis and c-axis parameter differences can be caused by the tensile stress in the plane of PZT films resulted from the thermal expansion mismatch during cooling [4].

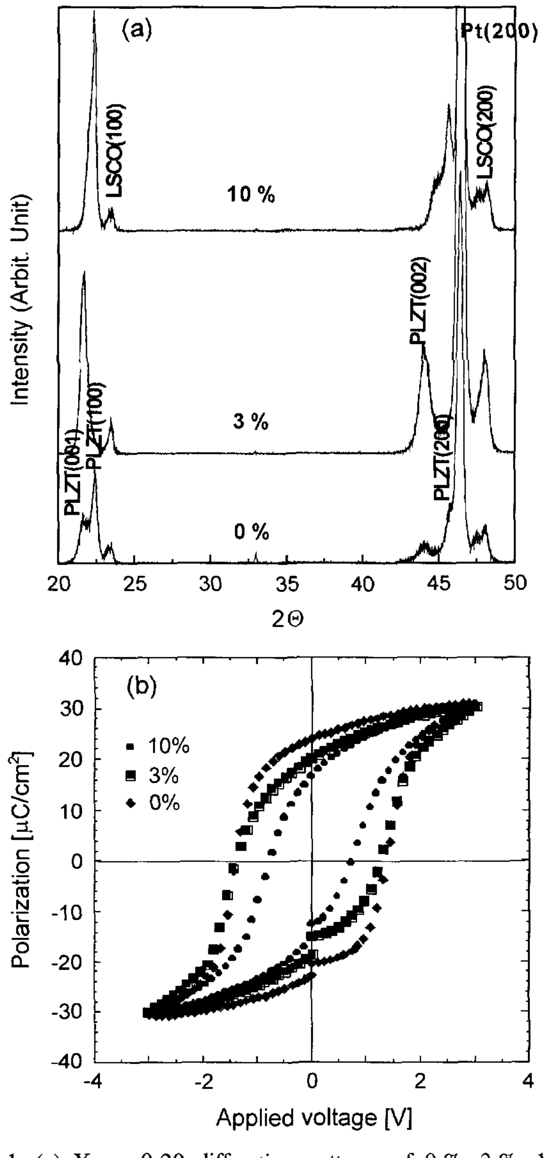

Fig. 1. (a) X-ray θ-2θ diffraction patterns of 0 %, 3 %, 10 % PLZT films on (100) Si/TiAlN/Pt/LSCO and (b) Hysteresis loops for 10 %, 3 % and 0 %-PLZT capacitors, measured at applied voltage of 3 V.

Hysteresis loops for 10 %, 3 % and 0 % La substituted films are shown in Fig. 1(b). Polarization of 10 % La substituted samples is only slightly changed in the applied voltage range of 1.5~3 V, but 3 % and 0 % samples show rapid decrease of pulsed polarization with decreasing applied voltage. This different behavior can be explained by the different domain structures. The hysteresis loops of tweed-like domains, which were reported by other group [5], in La substituted PZT bulks have a lower coercive field and a slightly lower remnant polarization, similar to those of the 10 %-PLZT films, than those of normal micron-sized ferroelectric domains. Consequently, the lower coercive voltage and slightly lower remnant polarization can be observed in 10 %-PLZT film due to different domain structures, compared to 0 % and 3 %-PLZT films. Therefore, the smaller distortion (lower c/a ratio) in 10 %-PLZT films leads to lower coercive voltages resulting from smaller depolarizing field.

This is an important indicator of the effect of La substitution on the switching characteristics of the ferroelectric film. The pulse polarization data show that although the hysteresis loops seem to indicate saturation at approximately 3 V, the capacitors with lower La substitution switch reluctantly at lower voltages. This difference in field dependent switching behavior can be understood through the effect of the c/a ratio on domain structures. For example, TEM studies of bulk PLZT show that in tetragonal [5] and rhombohedral [6, 7] PZT systems, the domain structure gradually changed from normal micron-sized domains through tweed-like domains to nanodomains with increasing La content. Thus, it is expected that the 10 % La PLZT thin films have a tweed-like domain structure while the 0% and 3 %-PLZT films have the normal micron-sized ferroelectric domains. As in the case of the bulk materials, this progressive change in domain structure with La substitution is a direct consequence of the effective c/a ratio of the tetragonal structure. The x-ray Bragg scans for our films clearly show that as La content is increased up to 10 %, the broadening of x-ray peaks due to splitting into a- and c-domains is gradually reduced. It has been reported earlier that the reduction of the x-ray broadening is a result of the change of domain structure towards nano polar domains [5]. Thus, the structural evidence

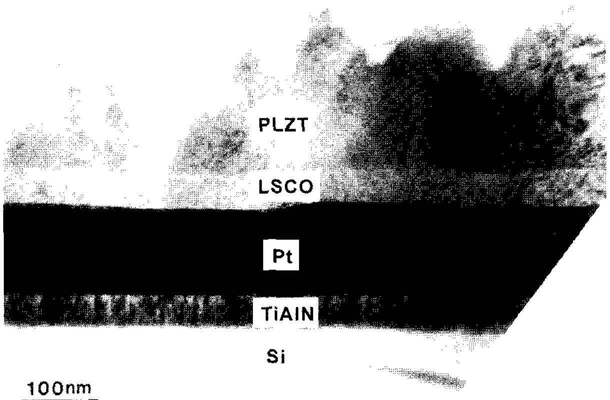

Fig. 2. Bright field TEM image of epitaxial LSCO/PLZT(10 % La)/LSCO/Pt/TiAlN heterostructure on Si (100).

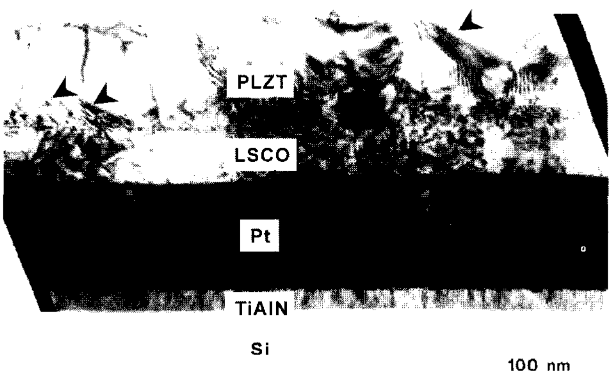

Fig. 3. Bright field TEM image of epitaxial PLZT (3 % La)/ LSCO/Pt/TiAlN/Si(100).

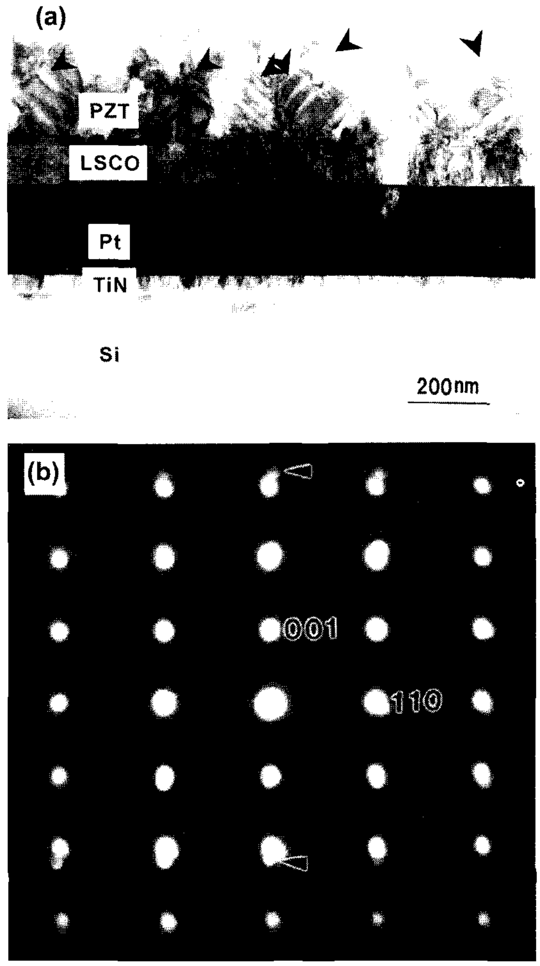

Fig. 4. Bright field TEM images of (a) epitaxial PZT(0 % La)/ LSCO/Pt/TiN/Si(100) and (b) diffraction pattern (B = [110]) for twinned regions in PZT.

strongly suggests that 10 %-PLZT films have the tweed-like domain structure.

TEM studies for PZT films with 10 %, 3 %, and 0 % La contents were performed to investigate the systematic variation of domain structures, as shown in Figs. 2, 3, and 4, respectively. The TEM image of PZT film with 10 % La content shows similar microstructure to the nanodomains of bulk PZT reported previously [5], which had very fine features inside the PZT. This sample also shows very clean interfaces, especially between PLZT and LSCO, and consequently no evidence for interaction between adjacent layers. However, TEM images of the PZT films with 3 % and 0 % La content show that much strain is involved in the PLZT and LSCO film, and high concentration of defects, such as dislocations, exists, especially in the interface between PLZT and bottom LSCO, compared to the PZT sample with 10 % La content. Arrows in TEM images of the PLZT films (with 3 % and 0 % La) indicate twin boundaries slanted to 45° with the film surface. The diffraction pattern using the [110] beam direction, shown in Fig. 4(b), clearly shows extra spots, indicated by arrows, due to 90° rotations of lattices resulting from twinning. These results from TEM observation confirm that the PLZT films with 3 % and 0 % La contents have 90° domains with twin structures.

Additionally, TEM studies reveal that there is no evidence of any reaction (or oxidation) products at the Pt (1200 Å)/TiAlN interface. This indicates that Pt/TiAlN barrier combination has superior oxidation resistance. Other evidence for domain structures in PLZT films with 0 %, 3 %, and 10 % La content can be found in the x-ray Bragg scan shown in Fig. 1(a). The x-ray Bragg scan clearly shows the existence of a-axis and c-axis oriented materials for 3 % and 0 %-PLZT, consequently implying the existence of 90° domains. As La content is varied from 0 % to 10 %, the broadening of x-ray peaks due to the splitting of a- and c-domains was gradually reduced. For instance, the lattice constant difference of a- and c-domains in the 10 % La-PLZT films was about 0.07 Å. This narrowing behavior of the width in x-ray peak as increasing La content up to 10 % is consistent with the observation in PLZT bulks [5]. Thus, it is confirmed that domains of 10 %-PLZT films have 180× domains. The direct correlation between the c/a ratio and the coercive voltage is important to note. The larger coercive voltage of 0 % and 3 %-PLZT samples seems to be related to the 90° domain structure in them, suggesting that switching of 90° domains is energetically more unfavorable compared to switching via 180° domains [8]. Consequently, the significant differences in domain structures (90° or 180° domains), resulting from the La addition portion into PZT capacitors, are reflected in the technologically relevant ferroelectric properties such as coercive voltages in polarization hysteresis measurements. Especially, features of the low coercive voltage for ferroelectric capacitors with 10 % La additions, due to the 180° domains structure, are especially important for low power and high speed memories.

4. Summary

The integration of ferroelectric capacitors with LSCO electrodes on Si using the $(Ti_{0.9}Al_{0.1})N/Pt$ conducting barrier composite has been demonstrated. A systematic change in the memory-relevant ferroelectric properties with La content, which result from the differences of ferroelectric domain structures, was also demonstrated. The beneficial effects of the controlled reduction in lattice parameters are clearly shown. Test capacitors with 10 % La additions show sufficient switched polarization at low voltage (1.5~3 V), resulting from fast switching behavior of 180° domains.

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