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Enhanced durability of designated polarization of $PbTiO_3$ nanodot arrays investigated by piezoresponse force microscopy

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ABSTRACT

We used piezoresponse force microscopy (PFM) to investigate local domain relaxation behavior of overhanging $PbTiO_3$ (PTO) nanodot arrays on platinized silicon substrates, which were prepared by using PbO vapor phase reaction sputtering on micellar monolayer films of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) loaded with TiO_2 sol–gel precursor. The overhanging PTO nanodot arrays (92% at a temperature of 100 °C for 365 min) showed better ferroelectric retention than the PTO thin films (80% at the same condition). The enhanced polarization states and the absence of depolarization field due to homogeneous electric field inside the overhanging nanodot allowed for the remarkable durability of designated ferroelectric polarization.

1. Introduction

Next generation nonvolatile memory devices require small bit size, long-term data retention and fast operating time [1,2]. Ferroelectric films have regarded as an outstanding candidate for such devices because a small electric field can polarize ferroelectric domains corresponding to a data bit and the data sustains without the electric field [3]. While ferroelectric random access memory (FRAM) based on the ferroelectric thin films is an everlasting topic in the nonvolatile memory community, considerable recent attention has been paid to investigating probe-based ultra-high density storage technology with ferroelectric materials [4]. Although there are massive efforts to develop ferroelectric thin films as the media for nonvolatile memory devices, the ferroelectric films may not be ideal for maintaining small domain size without collapse or crosstalk, which are serious obstacles to ultra-high density data storage [5,6]. To overcome inherently this instability, discrete ferroelectric nanostructures, such that one dot contains one bit exclusive of domain merging, have been recently prepared via various techniques including block copolymer self-assembly, anodic aluminum oxide (AAO) nanotemplate and dip-pen lithography [7–10].

An important issue in applying ferroelectric nonvolatile memories and data storage devices would be a polarization relaxation phenomenon, where progressive polarization loss reduces the bit signals corresponding to the two logic states: "1" and "0" [11]. Once the polarization loss begins, it expands lateral via the reversed domain [12,13]. This reduction makes distinguishing these different logic states difficult and decreases the reading ability of stored data. Although the retention characteristics of ferroelectric materials have been studied, most have been focused on ferroelectric thin films with switching dynamics or stability corresponding to the reduction of written polarization states [13–19]. Importantly, piezoresponse force microscopy (PFM) has been adopted as a powerful tool to explore local domain structures and switching behavior of the ferroelectric films at nanoscale. For example, W.S. Ahn et al. observed the retention loss phenomena of nanodomains with a diameter of 36 nm and square domains with a size of 1 and 25 μm^2 in $PbTiO_3$ (PTO) thin films fabricated by hydrothermal epitaxy on Nb-doped $SrTiO_3$ single crystals [16]. The retention loss was explained by the instability of the curved c^+/c^- domain wall and the compressive strain energy without leakage currents. A. Morelli *et al.* investigated polarization retention loss in single crystal PTO films grown by pulsed laser deposition onto $SrRuO_3/DyScO_3$ substrates by combination of PFM and conductive atomic force microscopy (c-AFM) [17]. They revealed that the presence of leakage currents was ascribed to the significant cause of polarization reversal. Furthermore, they also reported that the presence of defects at the electrode/film interface had an influence on the polarization retention loss [18,19]. Other studies in polycrystalline films suggested that the retention loss nucleated at grain boundaries and the reversed portion expanded laterally [12–15,20].

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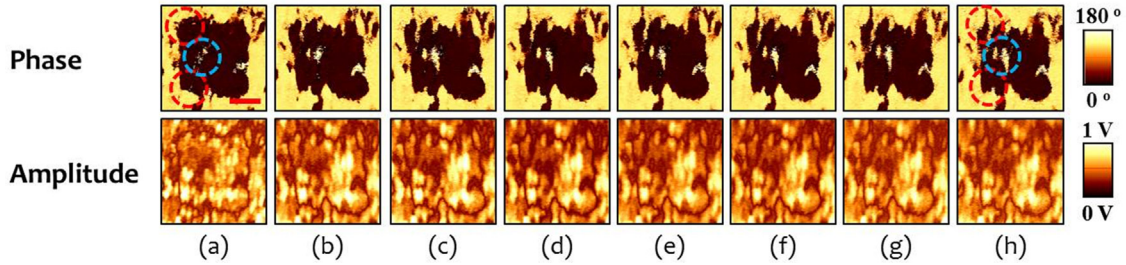

Fig. 1. Evolution of the tip-induced polarization of the box pattern in the PTO thin film over time: (a) poling, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min, (f) 80 min, (g) 110 min and (h) 170 min. Scale bar represents 200 nm.

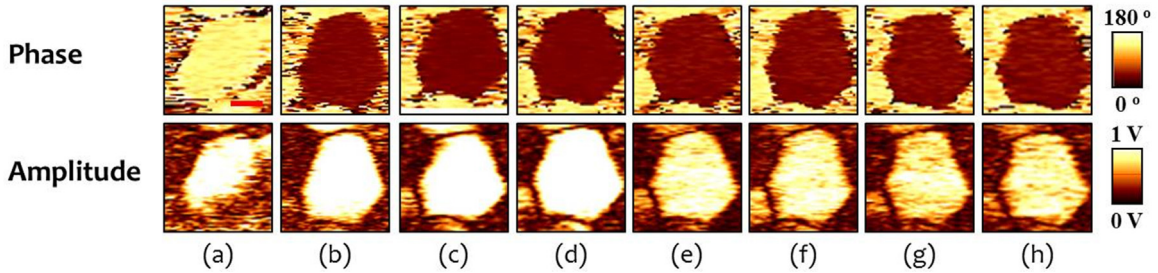

Fig. 2. Evolution of the tip-induced polarization of the PTO nanodot over time: (a) virgin, (b) poling, (c) 35 min, (d) 65 min, (e) 95 min, (f) 200 min, (g) 280 min, (h) 365 min. Scale bar represents 20 nm.

These studies, however, may not apply to domain evolution in the ferroelectric nanostructures since the electric field or polarization charge distribution of ferroelectric nanostructures is quite different from that of ferroelectric thin films. Accordingly, direct observation of ferroelectric nanostructures is crucial to determine whether they are useful for ultrahigh-density data storage with consistent stability of written domains. In this article, we firstly report the retention characteristics of ferroelectric PTO nanodots investigated by PFM.

2. Experimental procedure

Polycrystalline PTO thin films (20 nm in thickness) and PTO nanodot arrays (40 nm in height and 60 nm in diameter) were prepared on a platinized silicon substrate using PbO vapor phase reaction sputtering with TiO_2 seeds. Detailed fabrication conditions can be found in our previous works [10,21]. X-ray diffraction (XRD) analysis of the thin films and nanodot arrays confirmed the crystalline orientation of the PTO (1 0 0), (1 0 1) and (1 1 1) planes. In order to investigate retention characteristics, piezoresponse force microscopy (PFM) was used. PFM images were acquired using a commercial atomic force microscope (AFM, XE-100, Park System) equipped with a lock-in amplifier (SR830, Stanford Research Systems) [10,22]. An ac modulation voltage of 0.8 V_{rms} at 17 kHz was applied to the Pt-Ir coated AFM tip (CSC11 Ti-Pt, Micromasch) when acquiring phase and amplitude images of scanned areas. Initially, the PTO thin films were polarized from top to bottom with +5 V dc voltage at the tip over a scan area of 2 μm × 2 μm, a process is referred to as background poling. After the background poling, a small box pattern was written on the center of background poled area by applying −5 V dc to the tip over a 0.5 μm × 0.5 μm scan area. Differently, the designated PTO nanodots were polarized by nano-indentation with a pulse voltage of −8 V (same electric field used in the tip-induced poling of the thin films) and a pulse width of 1 s. Then, PFM images over a 1 μm × 1 μm scan area were obtained to examine the polarization states over time. The accelerated retention loss experiment was conducted by using a hot plate. Sample heating and PFM measurement were separated because the thermal noise from the heater made it difficult to measure *in situ* retention characteristics. The samples were heat treated at 100 °C in air and rapidly cooled down to room temperature before the measurement.

3. Results and discussion

Fig. 1 shows the evolution of the domain structure of the box pattern over time at 100 °C. Temperature accelerated testing accentuates the polarization relaxation process, enabling experimental measurements [23]. Dark and bright contrasts in the phase images correspond to domains oriented downward and upward, respectively. A 0.5 μm × 0.5 μm uniform polarized domain was created after poling and surrounded by 2 μm × 2 μm oppositely poled area, as shown in Fig. 1(a). Subsequently, the domain images were acquired at different time intervals after removing the external voltage and displayed in Fig. 1(b)–(h). We could observe a gradual decrease in the size of the written domain due to domain reversal. Reversed domains preferentially nucleated at domain boundaries, where the antiparallel orientation of the polarization encounters the edge of the box pattern. The lateral movement of the c^+ (upward

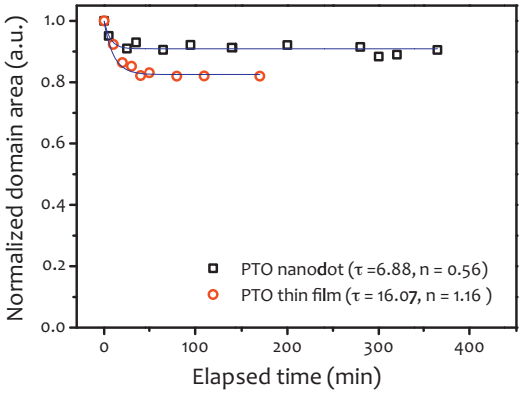

Fig. 3. Normalized domain area as a function of time. The solid lines below the normalized values denotes the exponentially fitted curves.