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# Nanoscale bit formation in highly (111)-oriented ferroelectric thin films deposited on glass substrates for high-density storage media

**Dae Hong Kim**[1], **Yong Kwan Kim**[2], **Seungbum Hong**[3], **Yunseok Kim**[4,5] **and Sunggi Baik**[1]

[1] Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Korea
[2] Semiconductor R&D Center, Samsung Electronics Co., Ltd, Hwasung, 445-701, Korea
[3] Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA
[4] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305-701, Korea

E-mail: sgbaik@postech.ac.kr

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**Abstract**

$PbTiO_3$ (PTO) ferroelectric films on Pt(111) bottom electrode layers covering Ta/glass were prepared using pulsed laser deposition. X-ray diffraction patterns revealed that the PTO films were preferentially (111)-oriented. The films were highly crystalline and had a smooth surface with root mean square (RMS) roughness of 1.5 nm. Ferroelectric properties of the PTO films were characterized using piezoresponse force microscopy (PFM). PFM techniques achieved ferroelectric polarization bits with a minimum width of 22 nm, which corresponds to a potential recording density of 1.3 $\mathrm{Tbit/in^2}$ in ferroelectric storage devices.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Most modern electronic data storage media are composed of magnetic materials. However, magnetic materials show superparamagnetic behavior when they are composed of very small crystallites [1]. As a result, the magnetization undergoes random thermal fluctuations which limit the capacity of high-density storage media [2–4]. The achievable recording density using perpendicular recording is believed to be between 500 $\mathrm{Gbit/in^2}$ and 1 $\mathrm{Tbit/in^2}$ [5–7]. Thus, to increase the recording density beyond this limit of magnetic storage media, information storage devices that use nonmagnetic material are required.

As an alternative to magnetic storage, a ferroelectric data storage system has been developed [8]. Ferroelectric materials have exceptional physical properties and therefore have a wide range of applications in electronic devices, including dynamic random access memories and nonvolatile ferroelectric random access memories [9–11]. Ferroelectric materials can have two different domains with opposite polarization states, as do magnetic materials [12]. In contrast to magnetic materials, the domain walls of typical ferroelectric materials are as thin as a few lattice parameters [13–15], which is suitable for high-density data storage media, because ferroelectrics do not have an analog of the magnetic exchange energy [16]. The very thin ferroelectric domain walls should allow recording densities far beyond those possible with magnetic media [17].

Ferroelectric materials have been integrated in the present hard disk drive (HDD) system with a field effect transistor sensing head to create a novel ferroelectric hard disk drive (FeHDD) that has a recording density that is far greater than the superparamagnetic limit imposed by the intrinsic thickness of magnetic domain walls [18, 19]. To obtain high recording density on ferroelectric materials, research has focused on

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[5] Present address: Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA.

single-crystal or epitaxial films [20–25], but commercialization of these materials is difficult due to the high cost of their single-crystal substrates. A glass substrate was therefore chosen here to replace the high-price single-crystal substrate. However, few studies have utilized glass substrate to achieve high recording density on ferroelectric materials.

The properties of ferroelectric films depend on the microstructure and texture of the films [26, 27]. Ferroelectric thin films with preferred orientation such as (001), (111), and (110) have better switching signals and lower operation voltages than randomly oriented ferroelectric thin films [28, 29]. Generally, (001)-oriented ferroelectric films have better fatigue resistance and reliability than do (111)-oriented ferroelectric films [30]. However, (001)-oriented $PbTiO_3$ (PTO) films are difficult to grow on glass substrates. In contrast, (111)-oriented PTO films are easily grown on glass substrates because Pt, which is typically used as a bottom electrode, can be grown with (111) texture and because the lattice mismatch between Pt and PTO along the (111) direction is only ~0.5% at room temperature [31, 32]. Moreover, in (001)-oriented ferroelectric films, many *c*-domains transform into *a*-domains during cooling after deposition, and this degrades the ferroelectric properties [33]. Therefore, (111)-oriented PTO is more suitable for data storage applications than is (001)-oriented PTO.

Here, we demonstrate the fabrication of preferentially (111)-oriented PTO thin films on Pt(111)/glass substrates. Nanoscale bit formation in this storage medium was investigated using piezoresponse force microscopy (PFM), and the minimum bit size was explored to test the maximum recording density in ferroelectric storage applications.

## 2. Experiment

The glass substrate used in this work was manufactured by Toyo Kohan Co., Ltd. Its root mean square (RMS) roughness is 0.15 nm and its average thickness is 0.63 mm.

### 2.1. Deposition of Ta and Pt

First, a 3 nm-thick Ta film was deposited on a 1 cm × 1 cm glass substrate using radiofrequency (RF) magnetron sputtering at 80 W RF power with 5 mTorr Ar gas at room temperature. The Ta layer increases the adhesion between the subsequent Pt layer and the glass substrate and improves the thickness uniformity of the Pt layer. Then a 20 nm-thick Pt electrode film was deposited on the Ta/glass substrates using RF magnetron sputtering at 20 W RF power with 12 mTorr Ar gas at 500 °C. A substrate temperature of 500 °C has been commonly used to improve both the adhesion and the crystallinity of Pt electrode layers [34].

### 2.2. Deposition of PTO

The PTO target was prepared using conventional ceramic powder processing. A powder mixture of raw materials ($1.05\ PbO + 1.00\ TiO_2$) was ball-milled for 12 h, calcined at 700 °C for 4 h, shaped into a disk of 2.54 cm diameter, and sintered in air at 1100 °C for 30 min. The 5 mol% excess of PbO was added to compensate for Pb loss during deposition. A 35 nm-thick PTO film was grown on the Pt/Ta/glass substrates using pulsed laser deposition at a substrate temperature of 550 °C with an oxygen pressure of 50 mTorr. A KrF excimer laser (wavelength 248 nm) was used with an energy of 120 mJ and a repetition rate of 2 Hz. Before film deposition, the deposition chamber was evacuated to a base pressure $<5 \times 10^{-6}$ Torr.

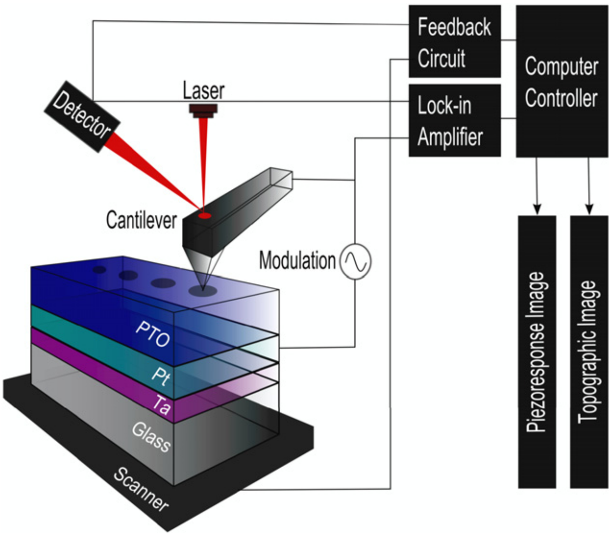


**Figure 1.** Schematic diagram of the layer stack on the glass substrate and AFM setup for measuring the piezoresponse signal in ferroelectric thin film.

### 2.3. Characterization

The crystal structure of the thin film was investigated using high-resolution synchrotron x-ray diffraction (XRD) at the 3C2 x-ray scattering beamline at the Pohang Light Source (PLS, Korea). A scintillation detector was used to record the diffracted beam intensities.

Domain switching and piezoresponse hysteresis loops were investigated (figure 1) using a commercial atomic force microscope (AFM) (SPA400, Seiko Inc.) connected to a lock-in amplifier (SR830, Stanford Research Systems) [35]. A conductive Rh-coated silicon tip served as a movable top electrode. The tip cantilever had a force constant of 12 N $m^{-1}$ and a resonance frequency of 135 kHz.

## 3. Results and discussion

The XRD $\theta$–$2\theta$ scan of the PTO film on Pt/Ta/glass (figure 2) showed strong Pt(111), PTO(111), and weak PTO(101) peaks on top of an amorphous background that was due to the glass substrate; the peaks demonstrate that the Pt film is (111)-oriented on the Ta/glass substrate because Pt is a face-centered cubic structure and the (111) plane has the lowest surface energy. The PTO film also has (111) preferred orientation because the lattice constant of Pt (3.92 Å at room temperature) differs from that of PTO by ~0.5% [31, 32]. However, the Ta

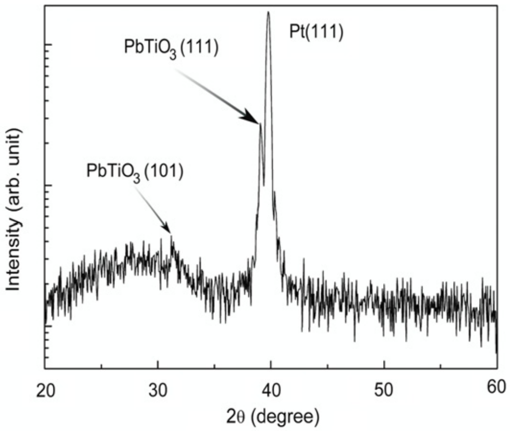


**Figure 2.** Synchrotron x-ray $\theta$–$2\theta$ scan of the PTO thin film grown on the Pt/Ta/glass substrate.

layer did not contribute peaks (figure 2) because it was too thin to generate a detectable signal.

Ta and Zr adhesion layers improve both the surface uniformity of the Pt electrode layer and its ferroelectric properties more than does the Ti adhesion layer, which has been mainly used on Si substrates [34, 36–38]. Ta and Zr adhesion layers should improve the uniformity and the ferroelectric properties of the film on an amorphous glass substrate such as $SiO_2$/Si. AFM images of Pt films deposited on Zr/glass and Ta/glass substrates (figure 3) confirmed that the Ta adhesion layer results in a smoother Pt electrode layer than does the Zr adhesion layer. From these images, the RMS roughness of the Pt film was 0.68 nm on the Ta/glass substrate and 5.48 nm on the Zr/glass substrate.

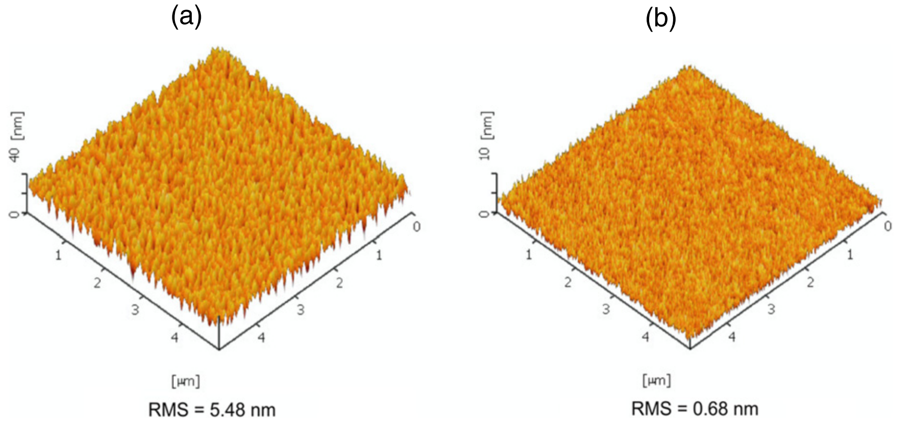
The surface morphology of the PTO thin film was observed using AFM as shown in figure 4(a). The RMS roughness over an area of 5 $\mu$m × 5 $\mu$m was ~1.5 nm with a peak-to-peak value of ~16 nm. To decrease bit size and protect the recording head during read/write events, the film surface must be very flat. The roughness of disk used in modern HDDs is ~0.3 nm [39]. However, RMS disk roughness on the order of 2–5 nm does not affect the distance between the surface of a disk platter and the read/write head [40]. Therefore, the 1.5 nm RMS roughness of the PTO thin film should be sufficient to allow the recording head to fly safely over the FeHDD media.

The recording performance of the FeHDD media was studied using PFM measurements, which have high resolution, can be conducted at ambient measurement, and can easily manipulate polarization states [41]. The PFM technique is based on the detection of the local electromechanical vibration of a ferroelectric sample caused by an external ac field. The obtained piezoresponse is $A\cos\varphi$ where $A$ is the tip vibration amplitude of the signal and $\varphi$ is its phase. $A$ is proportional to the piezoelectric coefficient, and the measured phase difference between the tip vibration signal and the applied ac modulation voltage indicates the direction of domain polarization.

The ferroelectric 180° domains, i.e. polarization pointing in opposite directions, are shown in the PFM images as dark and bright colors (figures 4(b) and (c)). Initially (figure 4(b)) a large area of 3 $\mu$m × 3 $\mu$m was switched downwards when $+6$ V was applied to the bottom electrode. This process is termed background poling. After the background poling, a small area of 1.5 $\mu$m × 1.5 $\mu$m was switched to upwards when $-6$ V was applied to the bottom electrode inside the background-poled area. Afterward, polarization directions were investigated using PFM. The PTO thin film was clearly switched at ±6 V. Furthermore, the entire measured area, including the as-grown region, had a strong piezoresponse and no secondary phase was observed.

The measurements of the local piezoresponse loops yielded the average $A\cos\varphi$, $A$, and $\varphi$ curves as a function of dc bias voltage (figures 5(a)–(c)). The coercive voltage $V_c$ was 1.7 V, and 180° ferroelectric phase switching occurred. Therefore, the ferroelectric property of the PTO thin films was confirmed.

To test the feasibility of using the PTO/Pt/Ta/glass structure as a high-density storage medium, bit size was varied by changing both writing time and pulse voltage. Bit arrays were written throughout the background area with $-6$ V as the tip bias was increased from $+6$ to $+10$ V while increasing writing times from 1 to 500 ms at each bit (figure 6(a)). From these writing time and voltage tests (figure 6(b)), controlled bit arrays and the bit size dependence on those parameters were obtained (figures 6(c)–(e)) [42]. The minimum bit



RMS = 5.48 nm

RMS = 0.68 nm

**Figure 3.** AFM topographic images and RMS roughness of the surface of Pt thin films sputtered on (a) Zr (3 nm)/glass and (b) Ta (3 nm)/glass.

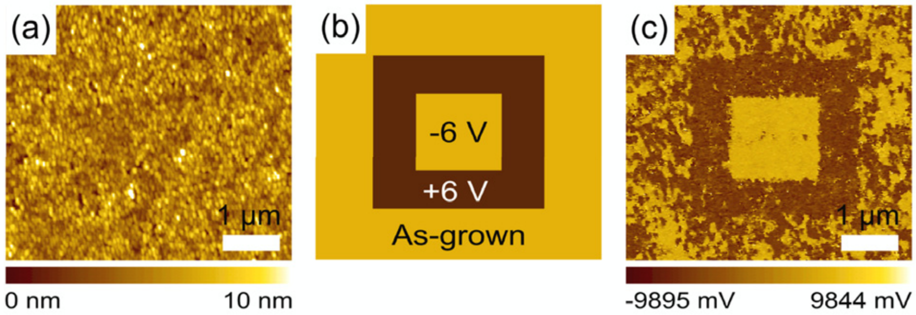


**Figure 4.** (a) AFM topography of the PTO thin film. (b) A domain formation scheme; box patterns (5 $\mu$m × 5 $\mu$m with a bias of +6 V and 1.5 $\mu$m × 1.5 $\mu$m with a bias of −6 V). (c) PFM phase image of the PTO thin film after domain switching by the scheme in (b).

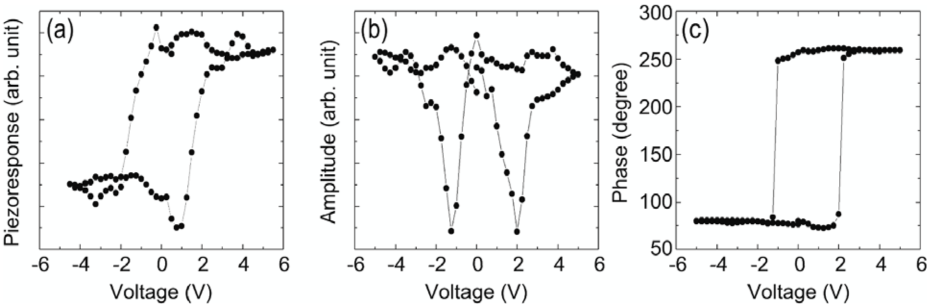


**Figure 5.** (a) Piezoresponse ($A \cos \varphi$), (b) amplitude ($A$), and (c) phase ($\varphi$) as a function of dc bias voltage applied to the bottom electrode. Completely switched domains are observed.

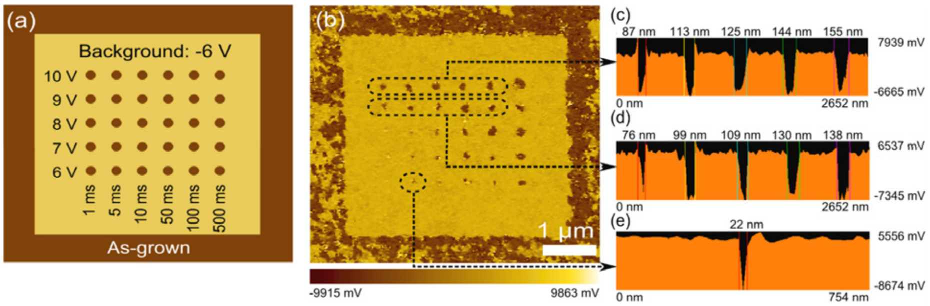


**Figure 6.** (a) A scheme for writing a ferroelectric dot array in a background area switched by a bias of −6 V. Various tip biases from +6 to +10 V were used with a writing time range of 1–500 ms. (b) The ferroelectric dot array formed by the scheme in (a). The size of bit array at (c) 10 V, (d) 9 V, and (e) minimum single bit size.

size was 22 nm, which gives a potential recording density of ~1.3 Tbit/in$^2$. The smallest bit size was determined by the radius of the conductive probe [21] which is about 20–25 nm. This minimum single bit size and recording density are beyond the standard bit size (39 nm) and recording density (416 Gbit/in$^2$) of modern HDDs. Thus, this result shows the feasibility of next generation FeHDD media. The bit size had a logarithmic relationship with writing time and decreased as the applied voltage decreased (figure 7). This plot indicates that the bit size can be <10 nm and the recording density can be > 6.5 Tbit/in$^2$ if the radius of the conductive probe can be decreased to 10 nm [43].

Finally, actual information storage ability was demonstrated by writing the line patterns periodically using voltage pulses of 50 ms with a pulse voltage of ±5 V. Even though the pulse generation was not well aligned, the repetition of ‘1’ and ‘0’ was sufficiently verified (figure 8(a)). This demonstration manually mimicked the HDD-type ferroelectric writing patterns. In writing signals corresponding to periodically inverted domain line patterns, the pitch between one polarity and the opposite one in the line pattern was ~77 nm (figure 8(b)), but can probably be decreased further using the over-writing technique [44].

## 4. Conclusions

We fabricated preferentially (111)-oriented PTO thin films on (111)-oriented Pt/Ta/glass substrates. These thin films exhibited a stronger switching signal and a small bit size than

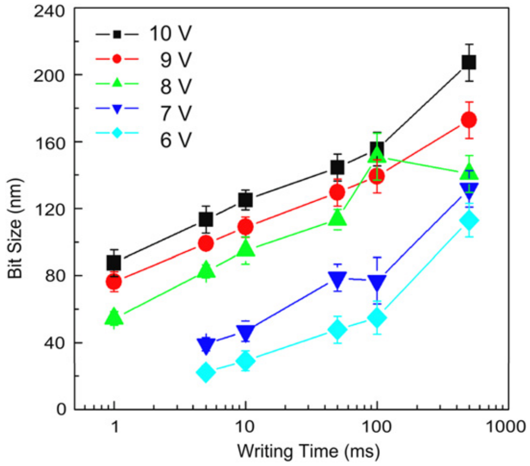


**Figure 7.** Plot of bit size versus writing time at various applied voltages.

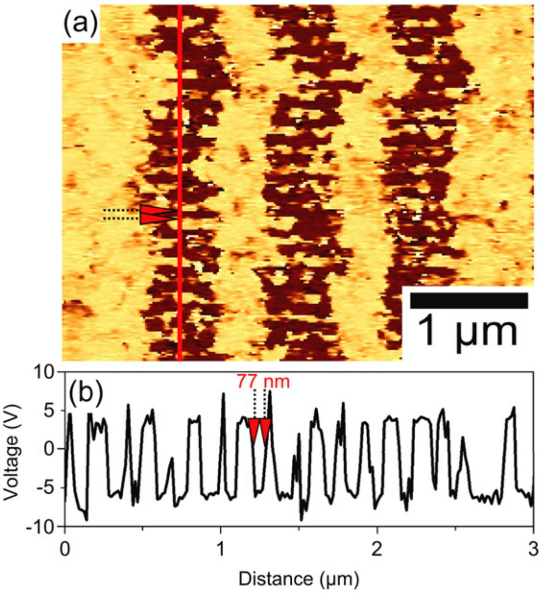


**Figure 8.** (a) PFM phase image of ferroelectric domains patterned with continuous lines on the PTO thin film. A pulse bias of −5 V was applied for 50 ms. (b) The PFM phase profile corresponding to the line in (a). The switched line patterned domains show a line width of ∼77 nm.

do randomly oriented ferroelectric thin films. The surface roughness (∼1.5 nm) of the PTO thin film should allow a read/write head to fly safely over the disk platter. Local area poling and hysteresis tests showed that the polarization states of the present films can be reversibly switched. The bit size can be easily and reliably controlled by applying voltage pulses to the films, and the obtained minimum single bit size of the sample was 22 nm, which corresponds to a recording density of 1.3 Tbit/in$^2$. This value is higher than the current limit for magnetic storage media. We obtained '010101' type data without destructive interference at the boundaries. The data in such a series can be read easily because they will, on average, give larger signals. These results indicate that use of (111)-oriented PTO thin film on Pt/Ta/glass as storage media for commercial FeHDD should be feasible and that this technique should be useful to obtain high recording density and to reduce production costs.

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