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Synthesis and characterization of $PbTiO_3$ Ferroelectric nanocrystals on atomically flat α-Al_2O_3 (0001) substrates by RF magnetron sputtering

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$PbTiO_3$ (PTO) ferroelectric nanocrystals were deposited on atomically flat α-Al_2O_3 (0001) substrates by RF magnetron sputtering. The atomically flat α-Al_2O_3 (0001) substrates were obtained by annealing the α-Al_2O_3 (0001) substrate for about 3 hours at 1000-1200℃ and the surface with atomic steps and terrace was observed by atomic force microscopy (AFM). In the RF magnetron sputtering method, high energy particles were sputtered on the substrates. Therefore, nucleation of crystals is stimulated at the atomic steps by control particles sputtered with high energy. Their particles were controlled by setting a cover material (α-Al_2O_3) on the substrates. Judging from the result of observations with XRD, XRF and AFM, the crystallized PTO nanocrystals were triangular in shape, with side length of 100-150nm and height of 20-30nm. In addition, it was confirmed by AFM that, when the cover allowed sputtered particles to approach ascending atomic steps, PTO nanocrystals fell into alignment along the atomic steps. So, it was found that relation between direction of steps and direction in which sputtered particles came flying were very important.

Key words: PTO, nanocrystal, atomically flat substrate, RF magnetron sputtering, AFM

1. INTRODUCTION

The market for personal digital assistants to accommodate coming ubiquitous society has expanded rapidly in recent year. The performance conditions for the telecommunications devices in the ubiquitous society are high speed drive, low power consumption, nonvolatility, high capacity, reliable, etc. Ferroelectric random access memory is one electric technology which can fulfill these conditions.

The ferroelectric thin films of perovskite oxide such as lead zirconate titanate $Pb(Zr_x, Ti_{1-x})O_3$ (PZT) have been widely investigated for use in new memory devices and micromachining applications. Therefore, PZT is applied to noncontact IC cards and nonvolatile memory. Comparing the performance of FeRAM and that of other types of memory, FeRAM equals or surpasses all memory types in some performances such as high speed, low power consumption and nonvolatility. However, FeRAM shows insufficient capacity and reliability. So, an increase of the capacity and improvement of the reliability are highly desired.

Recently, it was reported that the piezoelectric and the ferroelectric behaviors of ferroelectric nanostructures were different from those of thin films. Well-ordered nanocapacitors with lateral dimensions of several tens of nanometers were prepared by patterning thin films using microprocessing techniques such as electron beam (EB) lithography [1] and focused ion beam (FIB) milling [2]. The microprocessing techniques can produce periodic patterns of nanostructure with a desired size and shape. Such a process is called “Top-Down”. However, the surface of the thin films may be damaged and the ferroelectric properties may be degraded by microprocessing. Also, some microprocessing machines are very expensive and mass production of nanostructures is difficult. On the other hand, self-assembled processes called “Bottom-Up” can produce good quality nanostructures smaller than microprocessing techniques. And nanostructures produced by self-assembled processes are damage-free. Furthermore, expensive equipments such as microprocessing machines aren’t necessary. That’s why self-assembled processes have received wide attention and reporting by Wasa et al. [3, 4] and Nonomura et al. [5-7] and etc [8]. In these studies, atomically flat substrates (single crystals substrate) with atomic steps and terrace, are used for the lateral growth along a terrace between the surface steps. However, position control of nucleation and growth control of nanosized single crystals by self-assemble is very difficult and cannot be managed as easily as those produced by microprocessing techniques.

In this study, because of position control of nucleation and growth control of nanosized single crystals, $PbTiO_3$ (x=0) (PTO) nanocrystals were deposited on atomically flat α-Al_2O_3 (0001) substrates with covers by RF magnetron sputtering. The covers were used to control particles sputtered with high energy. High-quality nucleus formation and growth were expected by reducing depositional rates at the covers. The obtained crystals were observed by atomic force microscopy (AFM), and the mechanism of crystal growth was discussed.

2. EXPERIMENTAL

2-1. Fabrication of atomically flat substrates

Atomically flat α-Al_2O_3 (0001) single crystals were used as substrates. The miscut angle of these substrates was 0.3° (Kyocera corp.). Incidentally, a miscut angle results in surface tilting. Atomically flat α-Al_2O_3 (0001) substrates were obtained by annealing at 1000-1200 °C for about 3 hours in air by tubular furnace (Yamada Electric Co., Ltd.: TF-630-P). The details of the annealing conditions are shown in Table I. The surfaces of α-Al_2O_3 (0001) substrates were observed by AFM.

Table I. Annealing conditions for fabrication of atomically flat substrates.

Anneal temperature	Heat up time (600°C/h)	Hold time	Cool down time
1000 °C	1hour 40min	3hour	natural cooling
1100 °C	1hour 50min	3hour	natural cooling
1200 °C	2 hour	3hour	natural cooling

2-2. Synthesis of PTO thin films and nanocrystals

PTO thin films and nanocrystals were deposited on the center area and the edge area of atomically flat α-Al_2O_3 (0001) substrates at 600°C by RF magnetron sputtering, respectively as shown in Fig. 1. These sputtering conditions were summarized in Table II. And the covers (material: α-Al_2O_3, obliquity: 1°) as shown in Fig. 1 were used to control particles sputtered with high energy and deposit PTO nanocrystals. Specifically, the depositional rate was reduced by the covers and the particles sputtered as its energy coming down were stuck in between the covers and the substrate. Therefore, film thickness was continuously decreased. The continuous decrease of thickness was thought to contribute to an increase in size and number of nanocrystals.

In addition, the cover placing had two patterns, which direction allowed sputtered particles to approach descending atomic steps and ascending atomic steps, as shown in Fig. 2. Also, direction of steps was specified as shown in Figure 2. So, it might be expected that deposition of nanocrystals is easy, leading to easy stimulation of crystals nucleation at the atomic steps. However, crystal grain size control of nanosized single crystals was difficult.

Finally, the compositions and crystalline orientations of the PTO thin films were evaluated by XRF and XRD, respectively. The nanocrystals were observed with AFM (SPA400, Seiko Instruments Inc.).

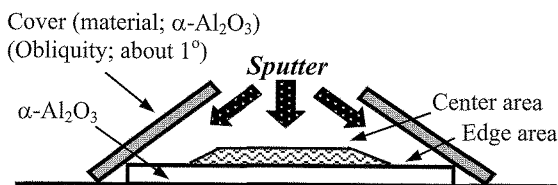

Fig. 1 Conditions of atomically flat substrates with cover in depositions of PTO nanocrystals by RF magnetron sputtering.

Table II. Sputtering conditions of PTO nanocrystals.

Target	$PbTiO_3$ Powder
RF power	100W
Substrate temperature	α-sapphire 600°C
Sputtering gas	Ar:O_2=9:1
Gas pressure	1.5Pa
Pre-sputter time	10min
Deposition time	30min

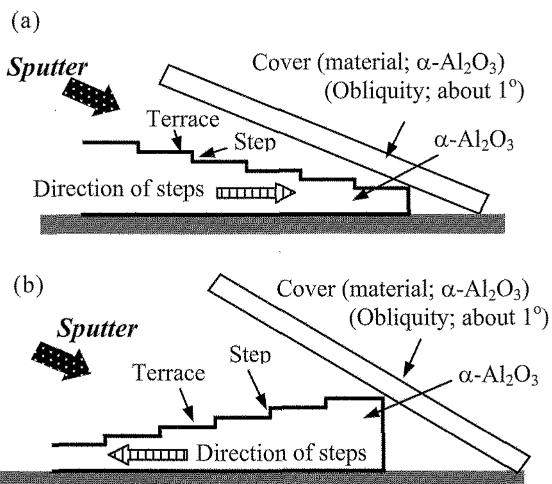

Fig. 2 Two patterns in cover placing along the direction to atomic steps: (a) direction that allowed sputtered particles to approach descending atomic steps and (b) direction that allowed sputtered particles to approach ascending atomic steps.

3. RESULTS AND DISCUSSION

3-1. Observation of atomically flat surface with atomic steps and terrace by AFM

A drastic change in the surface morphology of the sapphire wafers subjected to atomically flat treatment was observed, as shown in Fig. 3.

When sapphire substrates were annealed at 1000°C, atomically flat terraces were uniformly 40-45nm wide as shown in Fig. 3(a). The atomic steps were 0.22-0.44nm high. The height of 0.22nm is one atomic step height in α-Al_2O_3 (0001) single crystals [9]. The surface structure is thought to be stable and may contribute to deposition of high-quality thin films and nanocrystals.

Width of atomically flat terraces of substrates annealed at 1100°C in Fig. 3(b) was ranged from 40 to 150nm. The atomic steps were 0.22-0.88nm high ($i\times$ 0.22nm, i =1-10). The surface structure is thought to be a result of step-bunching [9] which had just begun and be unstable.

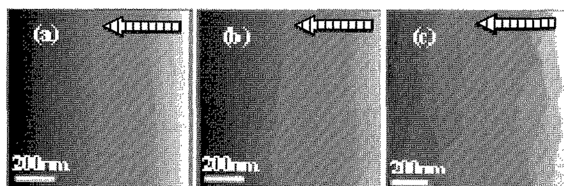

Fig. 3 Observations of atomically flat surface by AFM: annealing temperatures are (a) 1000 °C, (b) 1100 °C and (c) 1200 °C.

Atomically flat terraces of substrates annealed at 1200°C in Fig. 3(c) were irregularly 50-250nm wide. The atomic steps in Fig. 3(c) was 0.44-1.10nm high ($i\times$ 0.22nm, i =1-10). The surface structure is thought to be a result of step-bunching by atom migration at high temperatures and may contribute to nucleation of PTO at the atomic steps.

Those three substrates were used to deposit PTO thin film and nanocrystals.

3-2. Evaluation of PTO thin films by XRF, XRD

First, PTO thin films deposited on the atomically flat substrate (shown in Fig. 3) were evaluated by XRF, XRD. Composition ratio of Pb and Ti in the any PTO thin films was 1.2:1 (20% Pb rich) by XRF. Thickness of thin films was 100nm. XRD pattern of PTO thin films are shown in Fig. 4. PTO thin films only on the atomically flat substrate by annealing at 1000°C were found to be epitaxially grown form φ scan as shown in Fig. 5.

Also, PTO (111) peak and other phases like PbO (111) and pyrochlore peaks were observed on substrates annealed at 1100°C and 1200 °C. It is thought that those results were influenced by the surface condition of the atomically flat substrates, in other words, stable and periodic surface structure only stimulated PTO crystalline. So, single steps and flat terraces might contribute to deposition of the PTO epitaxial thin film.

In addition, because the number of φ scan peaks in the PTO was twice that in the α-Al_2O_3 as shown Fig. 5, it was determined that there were two different in-plane orientations in the PTO epitaxial thin film.

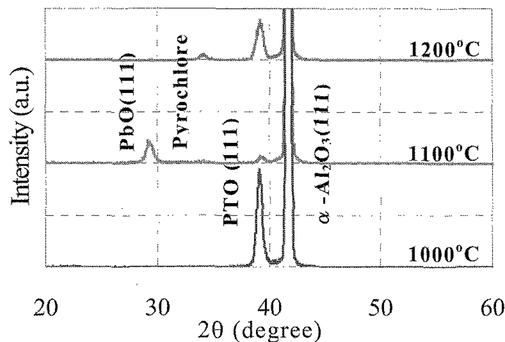

Fig. 4 XRD patterns: Substrate dependence in synthesis of PTO thin films on atomically flat substrate annealed at 1000°C ~ 1200°C.

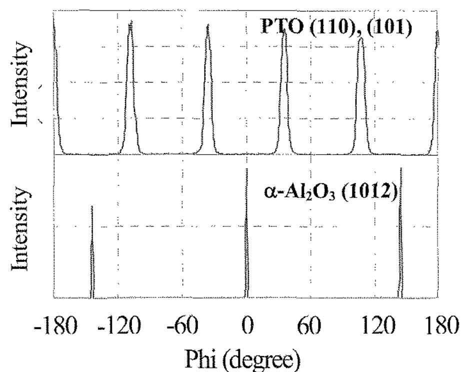

Fig. 5 φ scan of PTO thin films on the atomically flat substrate by annealing at 1000 °C

3-3. Observation of PTO nanocrystals by AFM

PTO nanocrystals were observed by AFM. Especially, PTO nanocrystals on the atomically flat substrate by annealing at 1000°C were investigated intensively because epitaxial PTO thin film was deposited. Fig. 6 shows the AFM image of PTO nanocrystals. Any AFM image has two triangular-shaped PTO nanocrystals placed symmetrically. This result agrees well with the XRD pattern (φ scan). Also, the side length and the height of the crystals were about 100-150nm and 20-30nm, respectively.

In the Fig. 6(a), when we pay close attention to the triangular-shaped crystals indicated by allows, we find there are no grains in the vicinity of the crystals. It is thought that an initial nucleus was formed and clumped together by migration of sputtered particles, resulting in larger triangular crystals. The density of nucleation increased greatly near the center area as shown in Fig. 6(b). Thus, position control of nucleation on the substrate without atomic steps is thought to be difficult.

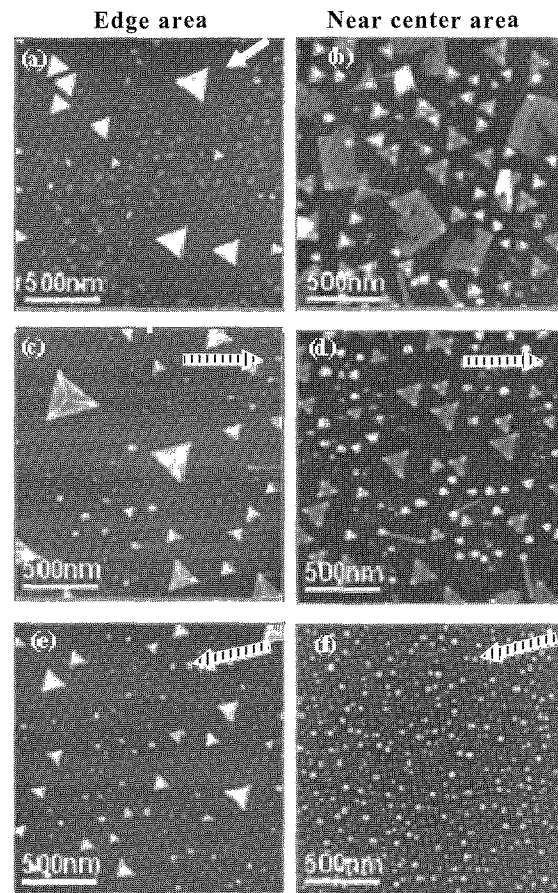

Fig. 6 AFM images of PTO nanocrystals: (a) and (b) on untreated α-Al_2O_3 (0001) substrates, (c) and (d) on atomically flat substrate with cover placed along direction allowing sputtered particles to approach descending atomic steps (shown in Fig. 2(a)), (e) and (f) on atomically flat substrate with cover placed along direction allowing sputtered particles to approach ascending atomic steps (shown in Fig. 2(b)).

In the Fig. 6(c), sputtered particles were thought to be

poorly suppressed by atomic steps because direction in which sputtered particles came flying was the same direction of steps. Leftward migration of sputtered particles, however, was suppressed by atomic steps. Therefore, few grains aligned along the atomic steps. The density of nucleation increased highly near the center area as shown in Fig. 6(d). So, it is thought that suppression of migration by atomic steps or optimizations of sputtering conditions are necessary for position control of nucleation.

In the Fig. 6(e), it was thought that sputtered particles were well suppressed by atomic steps because direction in which sputtered particles came flying and direction of steps were opposite. And rightward migration of sputter particles was suppressed by atomic steps too. The migration was suppressed more than that in the Fig. 6(c). That is why some grains aligned along the atomic steps. Additionally, many grains and nanocrystals got lined up along the atomic steps near the center area as shown in Fig. 6(f).

This result was also proved by the image of two dimensional fast Fourier transformation (FFT) of the Fig. 6(f), as shown in Fig. 7. The point of (18, 4), (-18,-4) indicated by allows in Fig. 7 is emphasized. Thus, the points show that there are nanocrystals aligned at 50nm intervals, which tilted by 12.5°, in the Fig. 6(f). The 50nm intervals are the same as surface terrace width of the atomically flat substrate by annealing at 1000 °C.

However, nanocrystals and grains tend to step over the atomic steps when the size of these crystals is bigger than the terraces wide. To solve this issue, it is necessary to reduce the miscut angle by polishing the α-Al_2O_3 substrates to widen the terraces wide. Therefore, synthesis of PTO nanocrystals controlled their positions by atomically flat surface with steps and terraces is thought to be possible.

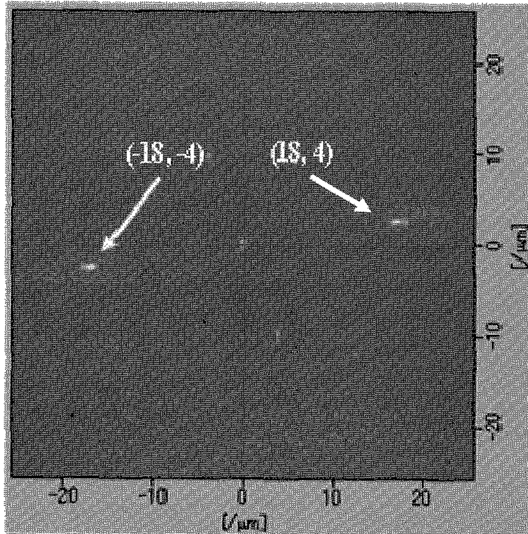

Fig. 7 The image of two dimensional fast Fourier transformation (FFT) of Fig. 6(f)

4. SUMMARY

PTO nanocrystals were deposited on atomically flat α-Al_2O_3 (0001) substrates with covers by RF magnetron sputtering. Especially, PTO nanocrystals on the atomically flat substrate annealed at 1000°C were confirmed to fell into alignment along the atomic steps when the cover allowed sputtered particles to approach ascending atomic steps. This is attributed to the fact that sputtered particles were well suppressed by atomic steps because direction in which sputtered particles came flying and direction of steps were opposite. So, we understood that relation between direction of sputter particles and that of steps was very important. Therefore, position control of nucleation is thought to be possible though RF magnetron sputtering.

In this study, growth control of nanosized single crystals was not studied well; that is to say synthesis of nanosized single crystals with uniformly crystal grain size on the whole substrate was difficult. In the future, we will go over the assignment.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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