Size Dependence of Ferroelectric Properties of Epitaxial PbTiO₃ Nanoislands on Pt/SrTiO₃(100)

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PbTiO₃ nanoislands were epitaxially grown on Pt/SrTiO₃(100) by self-assembly using metalorganic chemical vapor deposition. The width and height of PbTiO₃ nanoislands ranged from 30 to 200nm, and from 2 to 30nm, respectively. Piezoelectric constant ($d_{33,\text{PFM}}$) measured by piezoresponse force microscopy (PFM) rapidly decreased with the height when the height was less than 10nm, suggesting intrinsic size effects. PFM also revealed that the domain configuration was dependent on the width of nanoislands. The critical width for single domain was found to be 50nm.

Key words: PbTiO₃, nanoislands, size effects, self-assembly

1. INTRODUCTION

Recently, electronic devices with ferroelectric thin films, such as non-volatile memories and microelectromechanical system (MEMS) actuators and sensors, have been developed. One of key issues for high integration and low voltage operation of ferroelectric devices is a miniaturization of dimensions of ferroelectrics on substrates down to 100nm. Therefore, it is important to understand finite size effects in discrete ferroelectric islands fabricated on substrates. For example, the lateral size dependence of ferroelectric and piezoelectric properties of ferroelectric islands with lateral dimensions of 100nm-2 μ m fabricated by the top down methods has been investigated [1-3]. The size dependence was considered as extrinsic size effects derived from the clamping by substrates and 90° domain wall movements [1-3]. Intrinsic size effects, in these reports, were not observed because the dimensions of islands fabricated by the top down methods were much larger than the size in which intrinsic size effects were observed in ultrafine particles [4-6]. On the other hand, ferroelectric islands with dimensions similar to the critical size of ultrafine particles have been successfully fabricated by the bottom up method [7-10]. The critical size in PbTiO₃ nanoislands was found to be 20nm in width and 1.2-8nm in height [7,8,10]. However, the size dependence of ferroelectric and piezoelectric properties of nanoislands smaller than 100nm has not been well understood yet.

In this study, size dependence of piezoelectric constant and domain configuration in epitaxial PbTiO₃ nanoislands grown on Pt/SrTiO₃(100) by self-assembly were investigated by piezoresponse force microscopy (PFM).

2. EXPERIMENTAL PROCEDURE

SrTiO₃(100) single crystals were used as a substrate. In order to obtain an atomically flat surface with TiO₂-termination, SrTiO₃ was etched in a buffered

NH₄F-HF solution and subsequently annealed at 950°C in air [11]. The single-crystalline Pt films with a thickness of 30nm were prepared on SrTiO₃(100) by inserting 0.5nm-thick Ir layer into the interface between Pt and SrTiO₃(100) [12-14]. Pt thin films and Ir buffer layers were prepared at 550°C in an Ar pressure of 10mTorr by rf magnetron sputtering. Deposition rates of Pt and Ir films were 40 and 6.0nm/min, respectively. PbTiO₃ nanoislands were epitaxially grown on Pt/SrTiO₃(100) by metalorganic chemical vapor deposition (MOCVD). The growth temperature and pressure were 540-600°C and 5.0Torr, respectively. (C₂H₅)₃PbO-*n*-CH₂C(CH₃)₃, Ti(O-*i*-C₃H₇)₄ and O₂ were used as precursors and oxidant, respectively [13-15]. The surface morphology and piezoelectric properties were evaluated by atomic force microscopy (AFM) and piezoresponse force microscopy (PFM). Contact resonance PFM (CR-PFM) was also employed for observations of domain structure of PbTiO₃ nanoislands. A PtIr₃-coated cantilever with a force constant of 2.8N/m and a tip radius less than 25nm (Nanoworld: EFM) was used for both PFM and CR-PFM [16,17]. The resonance frequencies of the cantilever in non-contact and contact modes were typically 75kHz and 330kHz, respectively. In PFM, AC voltage with an amplitude of 1V_{pp} and a frequency of 13kHz was applied between the tip and bottom electrode to excite piezoelectric vibration of the sample. In CR-PFM, the amplitude of AC voltage applied to induce the flexural vibration in the contact mode was ranged from 0.1 to 0.5V. The frequency was chosen to be 3~10kHz lower than the contact resonance frequency of the cantilever.

3. RESULTS AND DISCUSSION

In thin film growth of PbTiO₃ by MOCVD, the growth mode was dependent on the underlying layer [18]. When Pt is used as a bottom electrode, PbTiO₃ is grown in the Volmer-Weber (V-W) mode. At the initial growth stage in the V-W mode, as shown in Fig.1,

Fig.1 A typical AFM image of $\text{PbTiO}_3(001)$ nanoislands on $\text{Pt/SrTiO}_3(100)$.

square-shaped nanoislands with a flat top surface were formed on $\text{Pt/SrTiO}_3(100)$ [14]. The dimensions of $\text{PbTiO}_3(001)$ nanoislands ranged from 2 to 30 nm in height and from 30 to 200 nm in width. The square nanoislands are suitable for quantitative analysis of piezoresponse because AFM tip can keep a stable contact on the flat top surface of nanoislands.

Figure 2 shows typical PFM images of PbTiO_3 nanoislands. PFM revealed that piezoresponse along the edge of individual nanoisland was larger than that on the center. For example, this is clearly observed in the nanoislands labeled as “A” in Fig.2(d). This enlargement of piezoresponse on the edges is not an artifact caused by topographic edge effects because this is observed independently of scanning direction, speed and the size of nanoislands. Therefore, the enlargement of piezoresponse can be considered as an increase in piezoelectric displacements on the edges of nanoislands. The difference in piezoresponse between the edge and center can be understood as follows. In the PFM imaging, the electric field is concentrated under a

Fig.2 Typical PFM images of $\text{PbTiO}_3(001)$ nanoislands on $\text{Pt/SrTiO}_3(100)$. (a,c) topographic and (b,d) PFM (amplitude) images. In island “A”, it is clearly seen that piezoresponse on the edge is larger than that on the center of nanoislands. Note that higher and smaller island “B” exhibits larger piezoresponse than island “A”.

conductive AFM tip used as a top electrode. This means that the resultant piezoelectric displacement is induced not in the whole nanoisland but just under the tip. Therefore, when the tip is positioned at the center of nanoislands, a region under the tip is restrained from the piezoelectric displacement by the surrounding area where the electric field and piezoelectric displacement are negligibly small. On the other hand, the restriction is

Fig.3 Dependences of piezoelectric constant ($d_{33,\text{PFM}}$) on (a) height and (b) width of PbTiO_3 nanoislands. $d_{33,\text{PFM}}$ was measured at the center of nanoislands. Open circles correspond to $d_{33,\text{PFM}}$ values of continuous films with thicknesses of 34–119 nm.

Fig.4 Relationship between domain configurations and (a) height and (b) width of PbTiO₃(001) nanoislands. All single domain nanoislands had a downward polarization.

less on the edge than at the center and larger piezoresponse is observed, as shown in Fig.2.

Considering the enhancement of piezoresponse on the edge, the size dependence of the piezoelectric constant ($d_{33,\text{PFM}}$) was investigated using the $d_{33,\text{PFM}}$ values measured at the center of nanoislands, as shown in Fig.3. The $d_{33,\text{PFM}}$ showed a distinct dependence on the height rather than the width of nanoislands. When the height of PbTiO₃ nanoislands was larger than 10nm, the $d_{33,\text{PFM}}$ was as large as those of continuous films, 25-45pm/V. This means that the $d_{33,\text{PFM}}$ of nanoislands higher than 10nm was determined by the constraint by the substrate. On the other hand, the $d_{33,\text{PFM}}$ drastically decreased from 30 to 5pm/V as the height decreased from 10 to 3nm. If the constraint by the substrate is responsible for the decrease of $d_{33,\text{PFM}}$ of nanoislands, the $d_{33,\text{PFM}}$ would show a dependence on the aspect ratio rather than the height, and would approach that of the continuous film with increasing the aspect ratio [19]. However, the $d_{33,\text{PFM}}$ of nanoislands was smaller than those of films and decreased with the height independently of the aspect ratio. This discrepancy suggests that intrinsic size effects have a larger influence on the height dependence of the $d_{33,\text{PFM}}$ than the constraint by the substrate when the height is less than 10nm. This is also supported by the fact that $d_{33,\text{PFM}}$ drastically drops when the height is less than 10nm, which is roughly equal to the critical size of PbTiO₃ ultrafine particles [4-6]. Note that the critical height below which piezoresponse is not shown should be below 2nm because the height of nanoislands was at least 2nm and all nanoislands exhibited piezoresponse in this study [7,8,10].

The size dependence of domain configurations was evaluated by CR-PFM, as shown in Fig.4. These nanoislands were consisted of only 180° domains. From Fig.4, it is found that the domain configuration is dependent on not the height but the width of nanoislands. When the width of PbTiO₃ nanoislands was smaller than 50nm, only a single domain with a downward polarization was found. On the other hand, 180° domains with two opposite polarizations were favored for

nanoislands with the width larger than 75nm. The domain structure of nanoislands develops to minimize the depolarization field after the phase transition from paraelectric to ferroelectric phases during cooling from the growth temperature [20-21]. The formation of 180° domains with two opposite polarizations reduces the depolarization field. However, the introduction of 180° domain walls simultaneously costs the energy. Therefore, the size dependence of domain configuration in PbTiO₃ nanoislands can be described as follows. In nanoislands smaller than 50nm, single domain minimizes a total energy because the introduction of 180° domain walls increases the energy; in nanoislands larger than 75nm, the depolarization field is successfully minimized by the formation of 180° domains with opposite polarizations.

In addition, the fact that all single domains were polarized downward implies a presence of surface charges at the ferroelectric phase transition. Fong, et al reported that, in MOCVD of ultrathin PbTiO₃ films, the direction of polarization was stabilized by adsorption of polar species, such as H, O, OH, H₂O and CO₂, on the surface [22]. In the growth of PbTiO₃ nanoislands by MOCVD, it is thought that these polar adsorbates also act as surface charges and have an influence on the direction of polarization. However, in this study, details of polar adsorbates still remain unknown because it is very difficult to experimentally specify the adsorbate on the surface of nanoislands.

4. CONCLUSIONS

Epitaxial PbTiO₃ nanoislands were grown on Pt/SrTiO₃(100) substrate by self-assembly using MOCVD. Square-shaped nanoislands with widths of 30-200nm and heights of 2-30nm were formed. The piezoelectric constant ($d_{33,\text{PFM}}$) rapidly decreased to 5pm/V as the height decreased to 2nm, suggesting the intrinsic size effects as well as the clamping by the substrate. From the size dependence of domain configuration, it was found that the domain developed to minimize a sum of depolarization field and 180° domain wall energies. The critical width below which single

domain was favored was found to be 50nm. All single domains had a downward polarization, suggesting that the direction of polarization was stabilized by polar adsorbates.

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