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Ferroelectricity of the 1.7 nm-high and 38 nm-wide self-assembled $PbTiO_3$ island

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Abstract

Crystalline and ferroelectric properties of nanosized $PbTiO_3$ islands grown at 390 and 560 °C by metalorganic chemical vapor deposition (MOCVD) were investigated by the grazing incidence X-ray diffraction (GIXD) method and piezoresponse scanning force microscopy (PFM). By reducing the growth temperature from 560 to 390 °C, average height of $PbTiO_3$ islands decreased from 19 to 3.6nm while the average width slightly decreased from 49 to 41nm. GIXD measurements revealed that nanosized $PbTiO_3$ islands with the pure perovskite phase were successfully grown at 390 and 560 °C. Preferential orientations of $PbTiO_3$ islands grown at 390 and 560 °C were (001) and (111), respectively. Using PFM, piezoelectric hysteresis loops with polarization reversal were obtained at each individual island. This is evidence for the presence of ferroelectricity in nanosized islands. The minimum island exhibiting ferroelectricity was 1.7 nm high and 38 nm wide.

Keywords: Ferroelectric properties; Films; Nanostructure; Perovskites

1. Introduction

Recently, many efforts have been made towards the high-integration of non-volatile ferroelectric random access memories (NV-FeRAMs). For example, 32Mbit NV-FeRAM with one transistor-one capacitor (1T-1C) cell architecture has been developed using a 0.25 μm design rule.[1] In the near future, nanosized capacitors will be required for the realization of Gbit-scaled NV-FeRAMs. Therefore, it is important to develop fabrication processes for nanosized ferroelectric capacitors and to understand their ferroelectric properties substantially including the size effects and the stability of ferroelectricity. There are two approaches to fabricate nanosized ferroelectric capacitors; (1) electron beam lithography [2,3] or focused ion beam milling [4] and (2) self-patterning of the electrode [5] or self-assembly of ferroelectrics.[6] Among them, the self-assembled crystal growth of ferroelectrics is advantageous in that complicated fabrication processes are not required to obtain nanosized ferroelectrics with both thickness and lateral dimensions below 50 nm. In an earlier study, we have already reported that self-assembled nanosized islands were obtained at the initial growth stage of $PbTiO_3$ and $Pb(Zr,Ti)O_3$ (PZT) thin films on $Pt/SiO_2/Si$ by metalorganic chemical vapor deposition (MOCVD).[6] Ferroelectricity of nanosized islands has also been proved by piezoresponse scanning force microscopy (PFM) observations.[7,8] In those studies, the minimum width and height of the $PbTiO_3$ island with ferroelectricity were 50 and 20 nm. However, this minimum size was not the critical size below which the ferroelectric state might be unstable, but determined by the growth conditions, such as the growth temperature and deposition time.

Recently, we have achieved the low temperature MOCVD of PZT thin films using nanosized $PbTiO_3$ islands as a seed.[9] It was also found that $PbTiO_3$ islands grown at temperatures lower than 450 °C were much smaller than those at 560 °C, in particular, in their heights.[9] For example, average width and height of $PbTiO_3$ islands prepared at 390 °C were 41 and 3.6 nm, respectively. However, it still remains unknown whether nanosized $PbTiO_3$ islands grown below 450 °C had ferroelectricity or not whereas they acted effectively as a seed for the crystal growth of PZT thin films.

In this study, crystalline and ferroelectric properties of nanosized $PbTiO_3$ islands grown at 390 and 560 °C are

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investigated. Ferroelectricity of the 1.7 nm high and 38 nm wide $PbTiO_3$ island prepared at 390 °C is also discussed.

2. Experimental procedure

Nanosized $PbTiO_3$ islands were grown on Pt(111)/ SiO_2/Si by MOCVD. Triethyl n-pentoxy lead ($(C_2H_5)_3PbO$-n-$CH_2C(CH_3)_3$), tetra-iso-propoxy titanium ($Ti(O$-i-$C_3H_7)_4$) and O_2 were used as source precursors and an oxidizing gas, respectively. The growth temperatures measured on Pt bottom electrode by an almel-chromel thermocouple were 390 and 560 °C. The growth rate calculated from the thicknesses of films deposited for 20 min was 11–12 nm/min at 390 and 560 °C. The deposition time of $PbTiO_3$ islands was 20 s. The out-of-plane and in-plane orientations of $PbTiO_3$ islands and films were examined by the conventional θ-2θ X-ray diffraction (XRD) and grazing incidence XRD (GIXD) methods, respectively. Piezoelectric hysteresis loops were measured on each individual $PbTiO_3$ island using piezoresponse scanning force microscopy (PFM). The elastic constant and resonance frequency of the $PtIr_5$-coated conductive cantilever were 2.8 N/m and 75 kHz. The frequency and amplitude of ac signals for the piezoelectric vibration were 10 kHz and 1.0–2.0 V_{pp}. Piezoelectric hysteresis loops were measured by sweeping dc bias voltage at 0.05–0.1 Hz simultaneously with ac signals.

3. Results and discussion

In the first stage, the orientation of $PbTiO_3$ films grown at 390 and 560 °C was examined. Fig. 1 shows out-of-plane XRD patterns of $PbTiO_3$ thin films deposited for 20 min. Diffracted peaks of perovskite $PbTiO_3$ were observed at the same positions as the bulk $PbTiO_3$. The preferential orientation of $PbTiO_3$ films changed from (100) to (111) as the growth temperature increased from 390 to 560 °C. This is because $PbTiO_3$ films were grown under a strong influence of the (111)-orientation of Pt bottom electrode when the growth temperature was 560 °C.

In the next stage, nanosized $PbTiO_3$ islands were prepared at the same growth conditions as those for $PbTiO_3$ films shown in Fig. 1. The deposition time was shortened from 20 min to 20 s. No diffraction peaks from $PbTiO_3$ islands were observed by the out-of-plane θ-2θ XRD method. On the other hand, diffraction peaks were successfully detected by the in-plane GIXD method, as shown in Fig. 2. From Fig. 2, it was found that $PbTiO_3$ islands grown at 390 and 560 °C had the pure perovskite phase. In the in-plane GIXD pattern of $PbTiO_3$ islands grown at 390 °C, (100), (110) and (200)-peaks were observed. Therefore, $PbTiO_3$ islands had only (001)-orientation in the out-of-plane as opposed to (100)-orientation of $PbTiO_3$ films shown in Fig. 1. This difference suggests that the orientation of $PbTiO_3$ grown at 390 °C is largely dependent on the thickness. In the GIXD profile of $PbTiO_3$ islands grown at 560 °C, (110), (101), (111), (200) and (211)-peaks were observed.

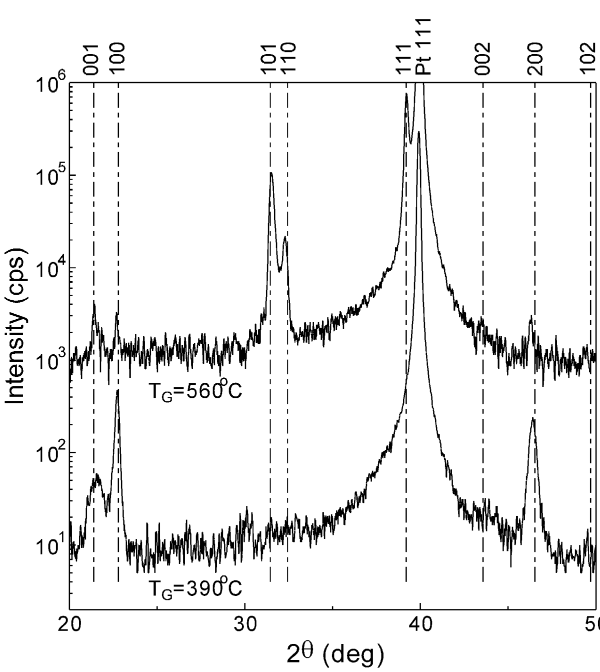

Fig. 1. Out-of-plane XRD patterns of 230 and 250 nm thick $PbTiO_3$ films grown at 390 and 560 °C, respectively. Dotted lines indicate 2θ angles of the bulk $PbTiO_3$.

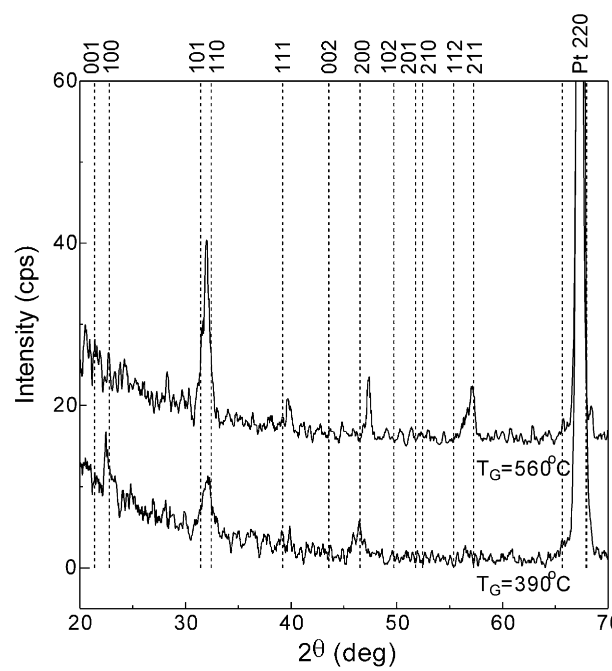

Fig. 2. In-plane GIXD patterns of nanosized $PbTiO_3$ islands grown at 390 and 560 °C.

These peaks indicate (111), (110) and (101)-mixed orientations in the out-of-plane direction. However, taking into account XRD patterns of $PbTiO_3$ films and the triangular shape of the $PbTiO_3$ islands observed in the AFM image [Fig. 3(b)], it was found that most of $PbTiO_3$ islands grown at 560 °C had (111)-orientation.

Fig. 3 shows AFM images of self-assembled nanosized $PbTiO_3$ islands grown at 390 and 560 °C. From Fig. 3(a), it was found that nanosized $PbTiO_3$ islands covered all over the surface when the growth temperature was 390 °C. On the other hand, relatively large $PbTiO_3$ islands were separately grown at 560 °C. The

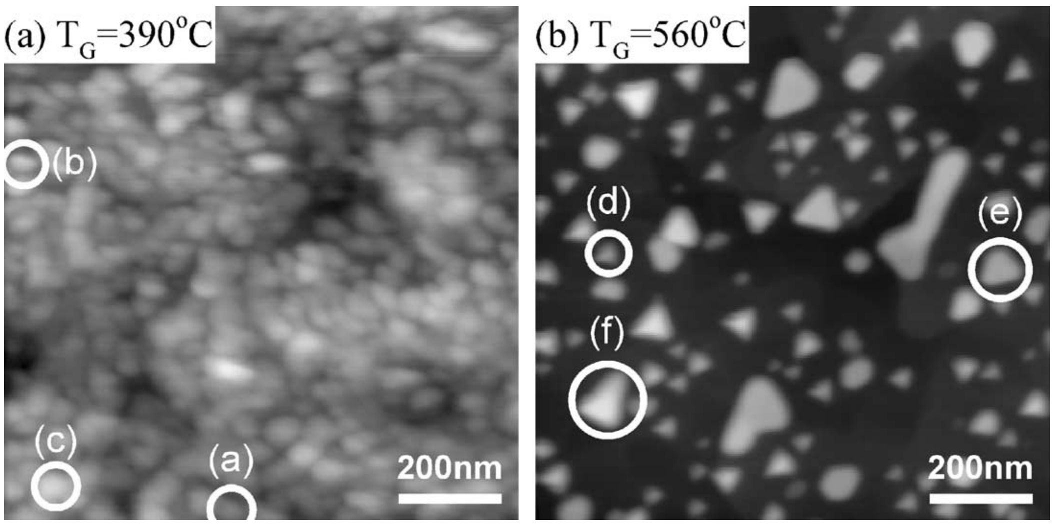

Fig. 3. AFM images of self-assembled nanosized $PbTiO_3$ islands grown at (a) 390 and (b) 560 °C.

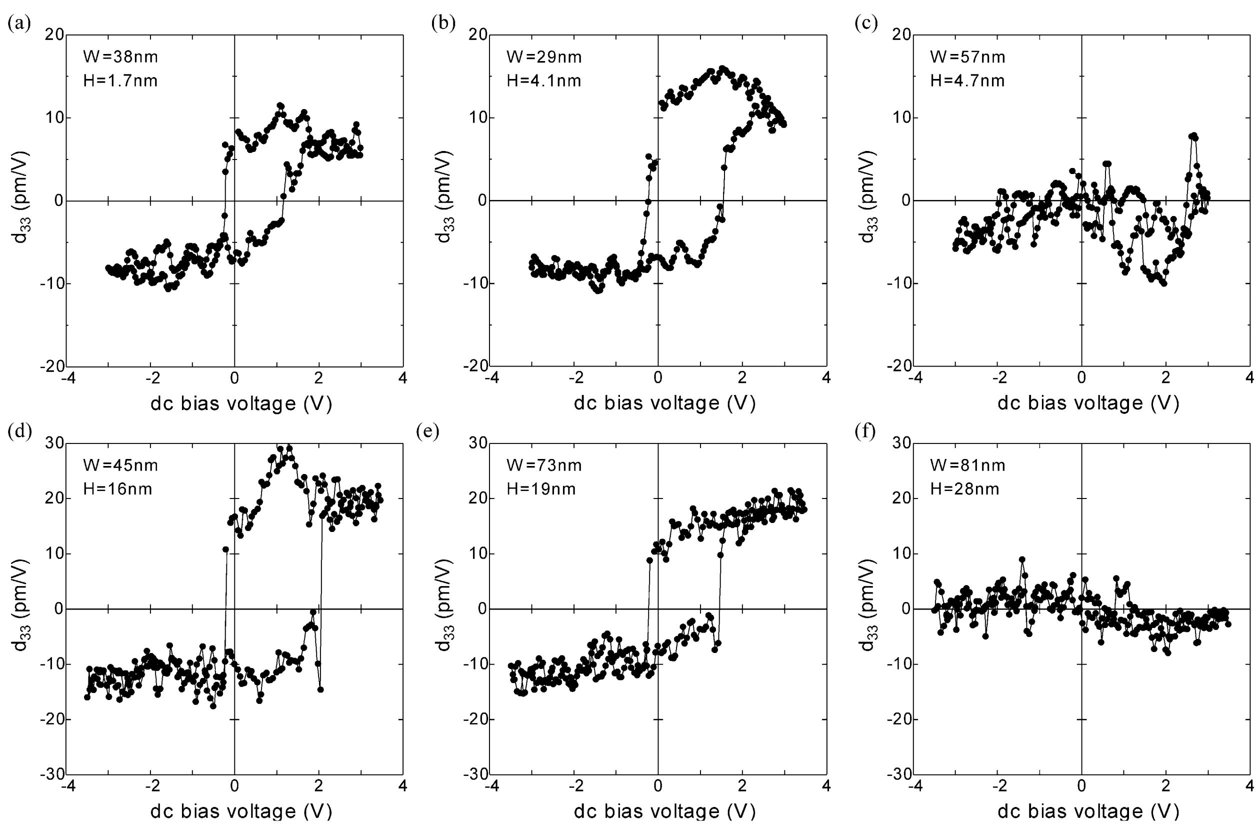

Fig. 4. Piezoelectric hysteresis curves; (a)–(f) were observed for nanosized $PbTiO_3$ islands which were encircled and labeled as (a)–(f) in Fig. 3. The widths and heights of islands are (a) 38 and 1.7 (the minimum height), (b) 29 (the minimum width) and 4.1, (c) 57 and 4.7, (d) 45 and 16, (e) 73 and 19, and (f) 81 and 28 nm, respectively.

triangular-shape of $PbTiO_3$ islands reflected the three-fold symmetry of the (111)-orientation, as mentioned above. Average widths and heights were 41 and 3.6 nm for $PbTiO_3$ islands at 390 °C and 49 and 19 nm for those at 560 °C, respectively. These AFM observations revealed that the height of islands decreased and the density increased as the growth temperature decreased from 560 to 390 °C. On the other hand, the width can be controlled by the deposition time because 2-dimensional growth was dominant in MOCVD growth of $PbTiO_3$.

The piezoelectric hysteresis curves are shown in Fig. 4. Fig. 4(a)–(f) was obtained in $PbTiO_3$ islands labeled as (a)–(f) in Fig. 3, respectively. For $PbTiO_3$ islands grown at 390 and 560 °C, piezoelectric hysteresis loops with polarization reversal were observed at 13 of 24 islands, and 18 of 32 islands, respectively, as shown in Fig. 4(a), (b), (d) and (e). These piezoelectric hysteresis loops evidently proved the presence of ferroelectricity. On the other hand, others did not exhibit ferroelectricity, as shown in Fig. 4(c) and (f). In $PbTiO_3$ islands without ferroelectricity, no piezoelectric vibrations were detected.

Piezoelectric hysteresis loops of ferroelectric $PbTiO_3$ islands were different from those of continuous films in following three points ; (i) shifts along both voltage and d_{33} axes, (ii) smaller d_{33} piezoelectric coefficient of 5–20 pm/V than that reported in 260 nm-thick film, 65 pm/V, [10] and (iii) extremely large coercive fields, 1-5MV/cm and 100–700 kV/cm for $PbTiO_3$ islands grown at 390 and 560 °C, respectively. Since these asymmetry or degradations of ferroelectric properties seem to depend on the size, we have examined the size dependence of these ferroelectric properties for $PbTiO_3$ islands including those grown at different growth temperatures and deposition times. However, no distinct size dependence of ferroelectric properties was observed, and details, including whether they are intrinsic or not, are now under further investigations.

The presence of ferroelectricity is plotted as functions of the width and height in Fig. 5. Piezoelectric hysteresis measurements were performed at 24 and 32 islands for $PbTiO_3$ grown at 390 and 560 °C, respectively. The $PbTiO_3$ island labeled as (a) in Fig. 3 had the minimum height of 1.7 nm (width = 38 nm) and the minimum volume of $1.9 \times 10^3 nm^3$, and that labeled as (b) in Fig. 3 had the minimum width of 29 nm (height = 4.1 nm), respectively. Piezoelectric hysteresis loops of these two islands were those shown in Fig. 4(a) and (b), respectively. It is surprising that the minimum height of 1.7 nm corresponds to only four unit cells of $PbTiO_3$. To our knowledge, these values are the minimum size of $PbTiO_3$ in which ferroelectricity was experimentally observed. In addition, in this study, piezoelectric hysteresis loops cannot be obtained at $PbTiO_3$ islands smaller than $1.9 \times 10^3 nm^3$ due to several difficulties in the measurements, such as a breakdown by high

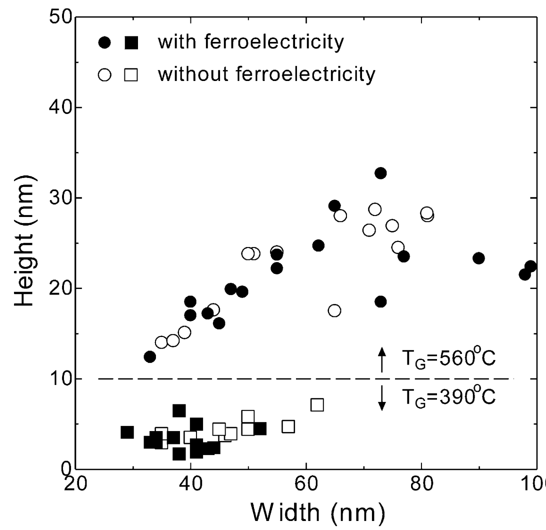

Fig. 5. The presence of ferroelectricity is plotted as functions of the width and height. Closed (■,●) and open (○,□) marks indicate $PbTiO_3$ islands with and without ferroelectricity. Squares (■,□) and circles (●,○) correspond to $PbTiO_3$ islands grown at 390 and 560 °C.

electrical fields (> MV/cm), degradation of the conductive coating of the SPM tip and the drift of the X–Y scanner. Therefore, the critical volume for ferroelectricity could be smaller than the minimum volume of $1.9 \times 10^3 nm^3$ obtained in this study.

The minimum volume of $1.9 \times 10^3 nm^3$ was three times larger than the critical volume of $6 \times 10^2 nm^3$ calculated from the critical size reported in $PbTiO_3$ fine particles, 10.7nm. [11] One reason for this is the difficulty in the measurements, as mentioned above. Another reason is a thermal strain derived from a difference in thermal expansion coefficients between $PbTiO_3$ and underlying Si substrate. For $PbTiO_3$ islands grown at 390 °C, a thermal expansion coefficient, $1 \times 10^{-5} K^{-1}$, of *a*-axis of $PbTiO_3$ in the temperature range 27–400 °C was much larger than that of Si substrate, $2.8 \times 10^{-6} K^{-1}$. Therefore, $PbTiO_3$ islands were subjected to an in-plane tensile stress at the room temperature. In fact, from Fig. 2, it was found that the in-plane *a*-axis of $PbTiO_3$ grown at 390 °C was elongated because (110) and (200)-peaks shifted slightly to lower angles than those in the bulk $PbTiO_3$. This elongation suggested shortening of the out-of-plane *c*-axis and consequent lowering of the spontaneous polarization as well as tetragonality. In the case of $PbTiO_3$ islands grown at 560 °C, the in-plane tensile stress also remains at the room temperature, although a formation of a–c multi-domain structures at the Curie temperature in the cooling process should be considered.[6] This lattice deformation might also cause degradations and asymmetry which were observed in the piezoelectric hysteresis loops, as shown above.

Therefore, it can be estimated that the critical size of nanosized islands was between the critical volume of 6

$\times$ 10^3nm^3 in fine particles and the minimum size of 1.9 $\times$ 10^3nm^3 obtained in this study.

4. Conclusions

Self-assembled nanosized $PbTiO_3$ islands with thickness and lateral dimensions below 50 nm were successfully grown on Pt/SiO_2/Si at 390 and 560 °C by MOCVD. Average widths and heights were 41 and 3.6 nm for $PbTiO_3$ islands at 390 °C and 49 and 19nm for those at 560 °C, respectively. Preferential orientations of $PbTiO_3$ islands grown at 390 and 560 °C were (001) and (111), respectively. Piezoelectric hysteresis loops proved that nanosized $PbTiO_3$ islands possessed ferroelectricity. The $PbTiO_3$ island with the minimum volume of 1.9 $\times$ 10^3nm^3, in which ferroelectric polarization reversal was observed, was 1.7 nm-high and 38 nm-wide. From the comparison of this minimum volume with the critical volume in fine particles, the critical volume of nanosized islands can be estimated to be between 6 $\times$ 10^2nm^3 and 1.9 $\times$ 10^3nm^3. These results also indicated that self-assembled nanosized ferroelectrics had a potential for NV-FeRAMs beyond Gbit densities.

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