In situ study of the evolution of domain structure in free-standing polycrystalline PbTiO$_3$ thin films under external stress

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The ferroelectric domain structure and its evolution with external stress in free-standing polycrystalline PbTiO$_3$ very thin films (VTF's) (thickness $t < 200$ nm) and thicker films ($t > 200$ nm), have been studied by *in situ* transmission electron microscopy. It is found that the domain structure of a VTF and its dynamic response to strain are remarkably different from those of a thicker film. The VTF is composed of nanosized grains, mostly single domained. These single-domained grains manifested a strong resistance against domain formation even under high stress. On the contrary, the thicker film is composed of larger grains, mostly multidomained. The domain structure in the thicker film changes significantly with external stress. The high stability of single domains in VTF's gives a satisfactory explanation to the abnormal electrical properties of VTF's compared with those of thicker films. [S0163-1829(97)02606-4]

I. INTRODUCTION

In recent years ferroelectric thin films have been intensively studied due to their promising applications in microelectronic devices.[1-3] It has been established experimentally that abnormal change of electrical properties, such as sharp increase in coercive field[4,5] and a drop in permittivity,[5,6] occurs when film thickness becomes very thin (e.g., $t < 200$ nm). These changes are of fundamental importance for the application of ferroelectric very thin films (VTF's). However, the reason has remained unclear up to now. Recently, it has been proposed that the thickness dependence of electrical properties may arise from some extrinsic reason, e.g., the presence of a surface layer of low ferroelectricity in series with a normal film,[5] but it seems more probable that such changes may be due to some intrinsic reasons.

It is well known that the electrical properties of ferroelectric materials are intrinsically determined by the domain structure and the mobility of domain walls. The coercive field is related to the easiness of domain nucleation and domain-wall motion; permittivity is related to the density of domain walls and their mobility at low field. It is thus very important to study the domain structure, and especially to study the dynamic behavior of domain walls under external field, such as electric or stress field. In recent years, there have been a number of studies devoted to the domain structure of ferroelectric thin films with thickness $t > 200$ nm.[7,8] However, little is known about domain structure in ferroelectric VTF's ($t < 200$ nm). The purpose of this paper is to clarify whether or not there exist some fundamental differences between ferroelectric VTF's ($t < 200$ nm) and thicker films ($t > 200$ nm) in domain structure and in dynamic response to external stress field. This may be a key to understand the intrinsic mechanism underlying the abnormal electrical properties of VTF's.

In the present study, we have used *in situ* transmission electron microscopy (TEM) to study the domain structures in PbTiO$_3$ thin films of different thickness ($t < 200$ nm and $t > 200$ nm) and their evolution with external stress or strain. *In situ* TEM technique has been known to be one of the most powerful tools for exploring dynamic processes under microscopic scale, and thus is expected to yield important microstructural information crucial for explaining the abnormal electrical behavior of ferroelectric VTF's. Despite the apparent importance of such an experiment, it seems that no *in situ* deformation experiment has been reported for ferroelectric thin films to date. This may be due to the difficulty in handling and stressing extremely fragile thin films. Fortunately, we have devised a way to perform *in situ* deformation experiment in TEM for unsupported PbTiO$_3$ thin films. In the following we shall report the experimental method and results.

It should be stressed that in this study we have used freestanding or supported thin films, thus the experimental results exclude the influence of substrates and electrodes which is inevitable in conventional studies and complicates the interpretation of the experimental result. Consequently the experimental results obtained here can be unambiguously explained in terms of intrinsic domain structure without being complicated by other factors such as substrates or electrodes.

II. EXPERIMENTAL

A. Specimen preparation

PbTiO$_3$ thin films with thickness ~ 80 and ~ 300 nm were deposited on NaCl substrates by using the sol-gel spin-coating method.[9] The 80 nm VTF was obtained by one coat, and 300 nm film was obtained by four coats. The details of the preparation procedure were described elsewhere.[10] In brief, the as-deposited films were pyrolyzed at 350 °C for 30 min in oxygen atmosphere, and followed by firing at 650 °C for 1 h to produce perovskite phase. X-ray-diffraction patterns showed that both 80 and 300 nm films were tetragonal perovskite, as indicated by the split of diffraction peaks. Dissolving away the NaCl substrates in water, we obtained unsupported thin films floating in water. The
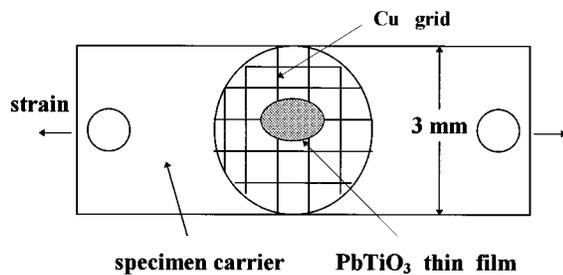
FIG. 1. Thin-film specimen for the TEM *in situ* elongating experiment.

free-standing thin films were collected on TEM copper grids, and the grids were then adhered to specimen carriers. Such a composite specimen, as shown in Fig. 1, can be mounted on a TEM elongating holder and deformed in the TEM. During the deformation of the grid, the thin film that was adhered to the grid was simultaneously deformed. The microstructure evolution *in the same region* under different strain was recorded on photographic plates. In this way we were able to carry out an *in situ* elongating experiment on TEM for free-standing PbTiO$_3$ thin films. This experiment was performed on a JEM-200 CX operated at 200 kV. It should be noted that the 80 nm thick VTF can be directly observed in TEM without thinning. For 300 nm films, a slight ion-milling (about 4–5 min) is necessary to get enough transparency.

B. Strain measurement

The average tensile strain in the thin films during elongation can be quantitatively evaluated by measuring the change of spacing between two grains along tensile direction. If the spacing before stressing is d and it changes into $d+\Delta d$ after stressing, then the average strain S is roughly given by $S=\Delta d/d$. In order to make accurate measurement the two grains are so chosen that they are distant from each other and have sharp grain boundaries. The uncertainty for the measured strain can be kept to less than 20% for careful measurement. It should be noted that the strain is not homogenous throughout the film because grain boundaries contain some amorphous phase (as will be shown in the next

section) and are generally ''softer'' than the interior of the grains. Consequently, the true strain inside a grain may be smaller than the measured mean strain.

It was found the thin films exhibit an unexpected ductility compared with corresponding ceramics. They can withstand a high strain up to 5% without fracture. Such a large strain may correspond to a large stress.

III. RESULTS

A. Difference in domain structure between VTF ($t\sim80$ nm) and thicker film ($t\sim300$ nm)

The microstructure of a crystallized PbTiO$_3$ VTF ($t\sim80$ nm) and that of a thicker film ($t\sim300$ nm) are shown in Figs. 2(a) and 2(b), respectively. It is clear that there exists much microstructural difference between the VTF and 300 nm film. It can be seen that the VTF is composed of very fine grains of about 60–80 nm in diameter, whereas the thicker film is composed of large grains with an increased size of 150–200 nm. A striking feature of the VTF compared with the thicker film is that most of grains do not show any domain pattern. This suggests that these grains are single-domained grains. Although the grain size in VTF is as small as ~60 nm, it is still much larger than the critical size for the formation of cubic perovskite, which was reported to be about 13 nm (Ref. 11) or smaller.[12] Therefore, the absence of domain patterns in VTF grains is surely not due to the formation of cubic perovskite. Statistics indicate that 82% of grains in the VTF are single domained, while 18% of them are multidomained. It is found that domain walls in multidomained grains are often irregular or curved, as indicated by the arrows in Fig. 2(a). On the other hand, in thicker films [Fig. 2(b)] multidomained grains are predominant, and most domains are lamellar. The domain width of multidomained grains in the VTF is about 5–20 nm, whereas it increases to be 15–50 nm for the 300 nm film. Almost all domain walls in both films appear to be 90° walls.

The VTF shown in Fig. 2(a) seems to exhibit a high microporosity, mostly at the junction of grains. However, careful examination into these ''micropores'' shows that they are mostly a very thin (<30 nm) amorphous layer. This is iden-
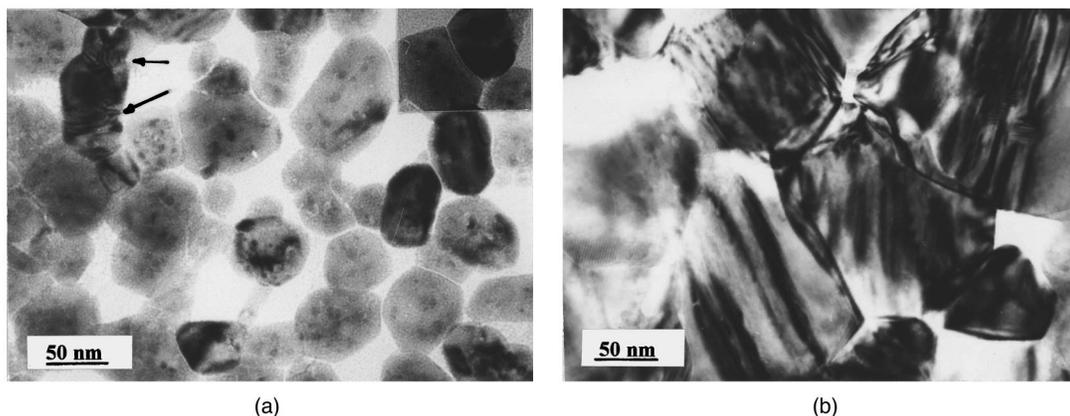

(a)

(b)

FIG. 2. The microstructure of PbTiO$_3$ thin films with different thickness. (a) very thin film (VTF) ($t\sim80$ nm), the rectangle portion on the upper right corner is overexposed so that the amorphous layer (with typical ''sand'' contrast) at the junction of grains can be clearly seen. (b) thicker film ($t\sim300$ nm).

tified by the weak ''sand'' contrast [as shown on the upper right corner of Fig. 2(a)] and by the unchanging of the contrast with specimen tilting. However, x-ray diffraction and electron diffraction show little sign of an amorphous phase. This may be due to the small fraction of such a phase compared with the perovskite phase. On the other hand, the thicker film [Fig. 2(b)] shows little amorphous phase as compared with the VTF. This fact indicates that VTF's may be difficult to completely crystallize.

B. Difference between VTF ($t\sim 80$ nm) and thicker films ($t\sim 300$ nm) in dynamic evolution of domain structure with external stress

The dynamic behaviors of the domains in VTF's and thicker films are found to be quite different, and they are described separately in the following.

1. In-situ elongation experiment on 80 nm VTF

It is interesting to observe the change of domain structure in ferroelectric VTF's with applied stress. Although the true stress cannot be measured directly, its magnitude can be roughly represented by the measured strain. Figure 3 shows an *in situ* TEM elongating result on an 80 nm VTF. The tensile strains for Figs. 3(a), 3(b), and 3(c) are 0, 1.1, and 5.0 %, respectively. From this figure, it can be seen that the domain structure, as a whole, does not show obvious change during deformation. It is found that single-domained grains and multidomained grains behave quite differently during deformation. Single-domained grains show an unexpected resistance against the formation of new domains. Despite the large strain or stress, we found a large majority of single-domained grains persist to be single domained without any sign of domain formation. Although the shades of some single-domained grains in Fig. 3 appear to be changed from gray into black (or *vice versa*) during deformation, it is not due to the domain change, but arises from the buckling of the specimen during deformation. The buckling may change the diffraction condition of some grains and thus change their contrast. As long as no typical ''strip'' contrast appears during deformation, the change of shades of grain cannot be considered a domain change. In fact, during *in situ* deformation, we have to continually adjust the focus knob to keep the image from blurring. This clearly shows that the specimen is really buckling during deformation. The high resistance against domain formation in single-domained grains suggests that nucleation of the domain is quite difficult in VTF's characterized by nanosized grains. Despite this, domains still form in a small number of single-domained grains during deformation, as in grain A and B shown in Figs. 3(a)–3(b).

In contrast to single-domained grains, multidomained grains in the VTF appear to be quite susceptible to external stress, and most of these grains exhibit some changes in domain structure. Some of them change into single-domained grains, as grain C shown in Figs. 3(a)–3(c) and some show a coarsening of domains, i.e., increase of domain width, as does grain D. It is found the domain coarsening is a general consequence of external stress for multidomained grains. Although domain structure changes significantly in multidomained grains, their influence on the electrical behavior of VTF's may be marginal, since the VTF is dominated by the
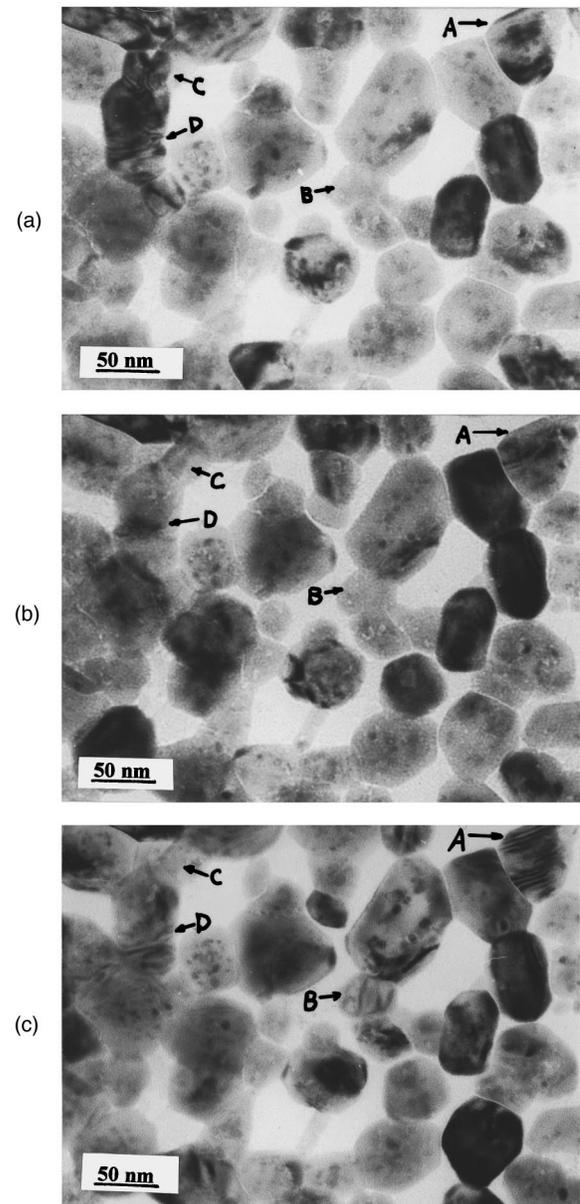

FIG. 3. The evolution of domain structure in PbTiO$_3$ VTF ($t\sim 80$ nm) under different strain. (a) $S=0$, (b) $S=1.1\%$, (c) $S=5.0$ %.

single-domained grains. Therefore, it is expected that the properties of the VTF's should mainly depend on the behavior of single-domained grains.

It is noteworthy that the maximum tensile strain has reached 5%, about an order of magnitude higher than the fracture strain of most ceramics. This suggests that a large portion of the strain in the VTF may be accommodated by the soft and thin amorphous layer, and only a small fraction is accommodated by the perovskite grains. Nevertheless, even though assuming the elastic strain accommodated by the perovskite grains is as small as about 0.1–1%, the electric field produced by this strain through the piezoelectric effect can still be calculated to be as large as 43–430 kV/cm from known elastic and piezoelectric constants of PbTiO$_3$. This is a fairly large field, but still not high enough to reverse the polarization of most of single-domained grains. This fact
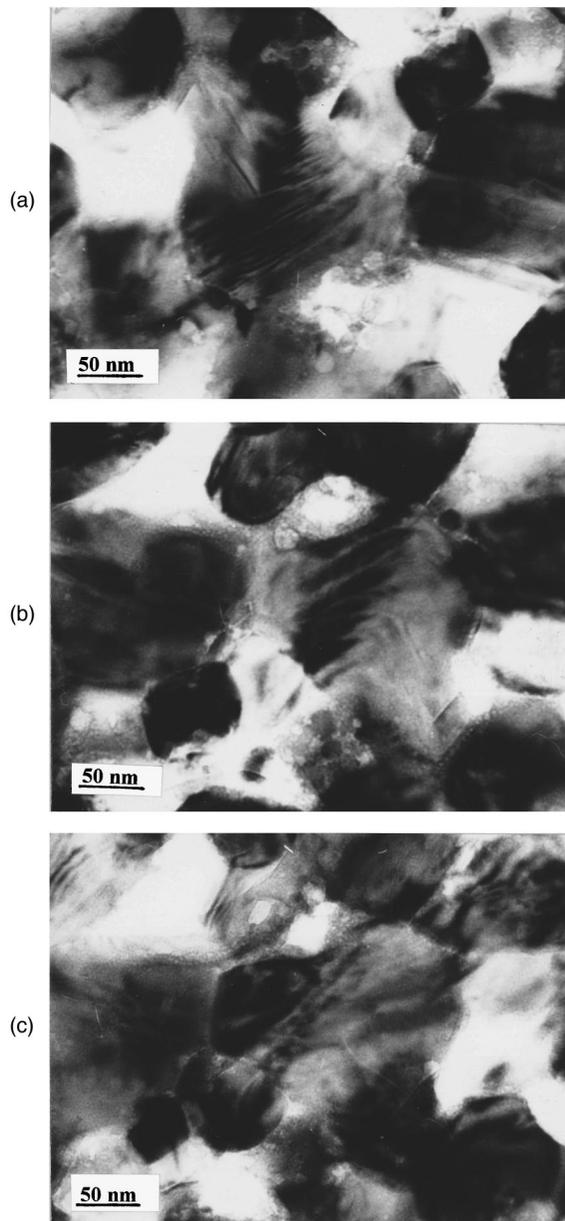
FIG. 4. The evolution of domain structure in PbTiO$_3$ thicker film ($t \sim 300$ nm) under different strain. (a) $S=0$, (b) $S=1.2\%$, (c) $S=4.5\%$.

indicates that the coercive field of this film is still larger. Therefore, the high stability of single-domained grains in VTF's under external stress explains the abnormally large coercive field (e.g., 1 MV/cm) of VTF's.

2. In situ elongating experiment on thicker PbTiO$_3$ film ($t \sim 300$ nm)

The dynamic behavior of the domain structure in the 300 nm film is found to be quite different from that in the 80 nm VTF. Figures 4(a)–4(c) show the evolution of domain structure with applied strain. It is clear that domain structure changes significantly when the film is strained. The lamellar domains continue coarsening with increasing strain, and ultimately change into coarse strips with faint contrast. This behavior is similar to the multidomained grains in VTF's, as

shown in Fig. 3 (grain D). It is found that the domain structure in 300 nm film shows appreciable change even at relatively low strain (e.g., 0.4–0.6 %). This suggests that the domain walls are quite mobile in this film compared with the VTF.

It should be noted that the 300 nm film is composed of coarse grains, and these coarse grains are mostly multidomained. Thus it is expected that the electrical behavior of the thicker film is mainly governed by the behavior of the predominant multidomained grains. In Fig. 4 it is shown that the domain walls in these grains have high mobility. This may lead to a reasonable explanation for the electrical behavior of such thicker films, as will be discussed in the next section.

IV. DISCUSSIONS

A. Thickness or grain size, which is the primary factor determining the domain structure of polycrystalline ferroelectric thin films?

In the past few years, much attention has been paid to the effect of film thickness on the electrical properties of polycrystalline ferroelectric thin films.[5,6,13–15] However, it has been found that even under the same processing conditions (such as firing time and temperature), change in film thickness can lead to a change in grain size. The thicker the film the larger the grain size.[5,16] This rule also holds in the present study, that is, the grain size of the 300 nm film [Fig. 2(b)] is much larger than that of the 80 nm film [Fig. 2(a)]. Thus, a question arises as to whether or not the observed thickness dependence of electrical properties is due to the inherent grain-size dependence. If considering that electrical properties are mainly determined by domain structure, we can change this question into an equivalent form: thickness or grain size, which is the primary factor determining the domain structure of polycrystalline ferroelectric thin films?

Many years ago, it was found that grain size has a strong influence on domain structure of ferroelectric ceramic.[17] This seems to suggest that grain size is the primary factor determining domain structure. In a recent paper[18] we have shown that domain structure still changes significantly with grain size even in the same film of uniform thickness. This gives a strong evidence showing that it is grain size, not the thickness, that determines the domain structure of the polycrystalline thin films, and consequently the electrical properties. In the present study, we also found that in a 300 nm film there exist a small number of tiny grains (50–80 nm) that are much smaller than the average grain size (150–200 nm). These tiny grains are mostly single domained, similar to the case in the 80 nm film with an average grain size of ~ 60 nm. This again manifests that grain size, not the thickness, is the primary factor governing the domain structure. The apparent thickness dependence of electrical properties is thus due to the inherent grain-size dependence of domain structure.

B. Reason for the anomalous electrical behavior of VTF's compared with that of thicker films

It is found in the present study that the domain structure of ferroelectric VTF's is quite different from that of thicker films. In VTF's single-domained grains are predominant

[Fig. 2(a)], indicating that single-domained grains are energetically more stable than splitting into domains. Most of these single domains even persist unchanged under a high stress or equivalently a high electric field, as shown in Fig. 3. On the contrary, in thicker films (>200 nm) multidomained grains are predominant [Fig. 2(b)], and domain structure can be easily changed by external field as shown in Fig. 4. The predominance of single domains in the nanosized grains of VTF's suggests that the single-domain state may be more stable than the multidomain state in such grains. Consequently, it is natural that formation of new domains in these grains is difficult and this is equivalent to a marked increase in coercive field. Similarly, due to the lack of domain walls in VTF's, the change of polarization due to domain-wall motion at low field is insignificant, and consequently the associated permittivity is small. Therefore, the sharp increase in coercive field and drop in permittivity in ferroelectric VTF's can be satisfactorily explained in terms of the stabilization of single-domained grains in VTF's, as found in our experiment. For thicker films ($t>200$ nm), because of the abundance of domain walls and its higher mobility, polarization reversal is relatively easier, hence the coercive field is much lower and permittivity is higher than that of VTF's.

In a recent TEM study[18] we have found that there exists a grain-size-related domain structure transition at a critical grain size of ~ 150 nm in polycrystalline $PbTiO_3$ thin films. When grain size is less than 150 nm, the domain structure is characterized by the predominance of single domains. In large grains (>150 nm), domain structure is characterized by the predominance of multidomains. Since film thickness is closely related to grain size as discussed above, it is natural that there should exist a critical film thickness (corresponding to the critical grain size) at which domain structure transition occurs, and consequently leads to an abrupt change in electrical properties at this thickness. The film thickness corresponding to the critical grain size ~ 150 nm is about 200–300 nm if the films undergo conventional heat treatment. Therefore, it is expected that domain structure transition occurs at film thickness 200–300 nm, and this thickness just coincides with the abrupt change of electrical properties of polycrystalline ferroelectric thin films.[4–6]

It is possible that the amorphous thin layer at the junction of grains as shown in Fig. 2(a) may also affect the properties of the VTF's. However, we believe it is only a secondary effect compared with the effect of the domain structure shown above. Similarly, the surface layer effect proposed by Sakashita and Segawa[5] may also be a secondary effect.

V. CONCLUSIONS

In the present study domain structure and its evolution with external stress in *free standing* polycrystalline $PbTiO_3$ thin films of different thickness were studied by *in situ* TEM. The following conclusions were obtained without being complicated by the influence of substrate and electrode.

(1) It is found that ferroelectric $PbTiO_3$ VTF's ($t\sim 80$ nm) are characterized by the predominance of single-domained grains, whereas thicker films (~ 300 nm) are characterized by the predominance of multidomained grains. Such a thickness-related domain structure change is closely linked to the grain-size driven domain structure transition through the thickness dependence of grain size.

(2) *In situ* TEM deformation experiment for VTF's has shown that the single-domained state remains stable even under high stress. For the 300 nm film, domain structure changes significantly with external stress, indicating the domain walls are quite mobile.

(3) The high stability of the single-domained state in VTF's gives a reasonable explanation for the high coercive field and low permittivity of these films compared with that of thicker films.

Finally, it should be pointed out that the observed film-thickness or grain-size dependence of the domain structure are intrinsic properties of polycrystalline thin films, thus it is expected that these dependences should generally hold when the films are supported (on substrates) or coated with electrodes.

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