

## Size-related ferroelectric-domain-structure transition in a polycrystalline $\text{PbTiO}_3$ thin film

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We studied the size dependence of the ferroelectric domain structure in unique free-standing  $\text{PbTiO}_3$  thin film, composed of grains 60–1000 nm in size, with transmission-electron microscopy. With such samples, we showed that the apparent dependence of electrical properties on the thickness of polycrystalline thin films stems from their grain-size dependence. We found that a domain-structure transition, from predominantly multidomain to predominantly single domain occurs at a grain size of  $\sim 150$  nm (corresponding to a thickness 200–300 nm). Based on these experimental results, the drastic change of coercive field and dielectric permittivity below a thickness 200–300 nm was reasonably explained as resulting from a domain-structure transition. [S0163-1829(96)50144-X]

Several decades ago, it was found that the electrical properties of ferroelectric powders are dependent on particle size.<sup>1,2</sup> With the extensive study of ferroelectric thin films in recent years, due mainly to their promising applications in microelectronic technology,<sup>3–5</sup> a similar size effect has also been found in ferroelectric thin films,<sup>6–8</sup> where the electrical properties show a dependence on the thickness of the films. Understanding the size effect in ferroelectric thin films is thus of both fundamental importance and essential for applications. Over the past few years there have been a number of studies<sup>9–13</sup> devoted to understanding the size effect in ferroelectric thin films, but the origin of some important experimental facts still remains obscure.

Perhaps the least understood experimental fact is the drastic increase of coercive field below a critical thickness (several hundred nanometers, depending on composition and processing condition, etc.), as has been found in some polycrystalline thin films.<sup>14</sup> Also, the observation of a marked drop in dielectric permittivity<sup>7,8</sup> below the same thickness has not been fully understood. Although it has also been argued that the thickness dependence of the electrical properties may arise from some extrinsic reason, e.g., the presence of a surface layer of low ferroelectricity in series with the normal film,<sup>7</sup> it is more probable that the change of properties is due to some intrinsic characteristic. The purpose of this article is to try to explore such intrinsic possibilities.

Intrinsically, the electrical properties are determined mainly by the ferroelectric domain structure and by the domain-wall mobility, as well as from the ease of domain nucleation. The strength of the coercive field is related to the ease of domain nucleation and domain-wall motion; permittivity is related to the density of domain walls and their mobility at low field. In order to understand the change of these electrical properties at small size, it is of vital importance to study the relation between domain structure and film thickness/grain size. However, no systematic study on the size dependence of domain structures in ferroelectric thin films, and especially its correlation with electrical properties, has been reported to our knowledge.

It should be pointed out that for polycrystalline films, grain size is a function of film thickness.<sup>7,15</sup> With an increase

of film thickness, the grain size increases. Thus a question arises as to whether or not the observed thickness dependence of electrical properties is due to their grain-size dependence, since grain size has been known to have a strong influence on the properties of ferroelectric ceramics.<sup>16</sup> In this paper we shall give a definite answer to this question by studying a deliberately prepared free-standing thin film sample ( $\text{PbTiO}_3$ ) composed of grains of vast difference in size (60–1000 nm) *in the same film*. In this unique thin film sample of fixed thickness we shall observe whether or not domain structure changes with grain size. If domain structure does not change with grain size, it means that domain structure and consequently the electrical property is solely controlled by thickness. If the reverse is true, it means that grain size, rather than thickness, is the controlling factor determining domain structure and electrical properties. By studying this unique thin film sample it is possible to obtain a reliable result about the grain-size dependence of domain structure, because all grains are in the same film. The observed grain-size dependence of domain structure can be used to interpret the thickness dependence of electrical properties because thickness is related to grain size as mentioned above. In the following we shall present the experimental procedure and results.

A  $\text{PbTiO}_3$  thin film ( $\sim 100$  nm thick) was deposited on NaCl substrate by sol-gel method. The film was preheated at 300 °C for 10 min in an oxygen atmosphere to pyrolyze residual organics, and followed by firing at 650 °C for 1 h to produce the perovskite phase. X-ray diffraction spectra showed that the film was tetragonal perovskite (ferroelectric phase), as indicated by the split of diffraction peaks. A free-standing film was obtained by dissolving away NaCl substrate in water. It was then collected on a copper mesh of 3 mm in diameter and studied in the transmission electron microscope (TEM). The TEM experiment was carried out on a JEM-200CX operated at 200 kV. The unsupported  $\sim 100$ -nm-thick  $\text{PbTiO}_3$  thin film, free from the influence of substrate, can be directly observed under the TEM without further thinning. It was found that the film was polycrystalline and had no obvious preferred orientation. The film had a homogenous grain size with an average diameter of about 60 nm.

A critical step is to make a thin film with different grain sizes while keeping the film thickness constant. This was done by the following way: removing the condenser lens aperture of the TEM and adequately converging the electron beam, yielded a high-intensity electron beam. Such an intense beam acted as a heating source ( $\sim 3 \mu\text{m}$  in diameter), and made the heated grains growing very fast. The grain size in the beam-heated area could be controlled by changing heating time and beam convergence, so that grains with sizes ranging from 60 to 1000 nm were obtained at different places *in the same film*. It was found that the grain growth was essentially in the plane of the film, thus the thickness of the film did not increase obviously during the beam heating.

Figure 1(a) shows a low magnification micrograph of a beam-heated  $\text{PbTiO}_3$  thin film, in which grains of vast difference in size are seen in the same film. Along the arrow direction, grain size changes from 1000 to 60 nm, the latter being the size of unheated grains. Figures 1(b), 1(c), and 1(d) are higher magnification micrographs of different portions of Fig. 1(a), corresponding to grain sizes of  $\sim 1000$ ,  $\sim 150$ , and  $\sim 60$  nm, respectively. We can see an interesting dependence of ferroelectric domain structure on grain size. Figure 1(b) shows the typical domain structure of  $\sim 1000$  nm grains. The zebra-like  $90^\circ$  domains are clearly seen. The domain width is measured to be 70–200 nm in these large grains. The domain structure found in these large grains is in fact very similar to that found in ferroelectric ceramics, which is characterized by large grains (usually several microns). Figure 1(c) shows the domain structure in  $\sim 150$ -nm grains. A lamellar domain structure can be seen, with a decreased domain width 10–50 nm. For grains smaller than 150 nm, domain structure changes drastically. For example, in Fig. 1(d) small grains of  $\sim 60$  nm show very different domain structure compared with that of larger grains shown in Figs. 1(c) and 1(d). Domain patterns are rarely seen in these small grains. This means single-domained grains are predominant at small grain size. The absence of domain patterns in small grains ( $\sim 60$  nm) cannot be rationalized by the fact that small grains have a cubic structure rather than a tetragonal one, since a 60-nm grain is too large for cubic  $\text{PbTiO}_3$  to form at room temperature (the critical size for cubic  $\text{PbTiO}_3$  formation at room temperature is reported to be<sup>17</sup> around 13 nm or smaller<sup>18</sup>). In addition, we have performed x-ray diffraction on fine-grained ( $\sim 60$  nm) thin film, and found the split diffraction peaks, an apparent evidence for the existence of tetragonality or ferroelectricity.

Figure 1 showed that the ferroelectric domain structure is strongly dependent on grain size despite that film thickness is fixed. This leads to an important conclusion: for polycrystalline thin films, grain size, rather than thickness, is the controlling factor determining domain structure and consequently electrical properties. The observed thickness dependence of electrical properties is thus due to the grain-size dependence, since thickness has one-to-one correspondence with grain size under the same processing conditions.

From Figs. 1(b) through 1(d) it is noticed that there exists a domain structure transition from multidomain predominance to single-domain predominance at a critical grain size. For  $\text{PbTiO}_3$  polycrystalline films the critical grain size for domain structure transition is about 150 nm. Such a

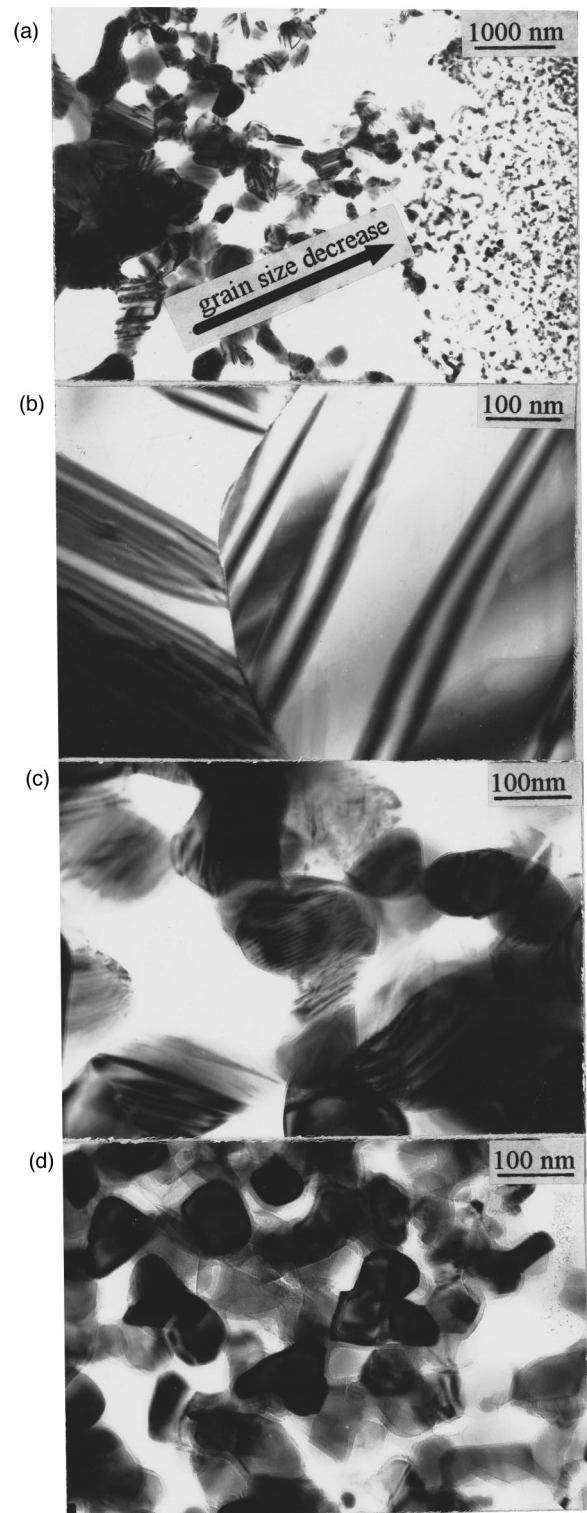


FIG. 1. Grain size dependence of domain structure in a free-standing  $\text{PbTiO}_3$  thin film composed of grains ranging from 1000 to 60 nm in diameter. Large grains are produced by electron beam heating. (a) Low magnification overview. Direction of decreasing grain size is arrowed. (b) Domain structure of  $\sim 1000$ -nm grains. Domain width: 70–200 nm. (c) Domain structure of  $\sim 150$ -nm grains. Domain width: 10–50 nm. (d) Domain structure of  $\sim 60$ -nm grains. Domain patterns are rarely seen.

grain size, under conventional processing condition (say, crystallization at 650 °C), corresponds to a thickness of 200–300 nm.

In very thin polycrystalline films, or equivalently fine-grained films, single-domained grains are predominant, indicating that single-domained grains are energetically more stable than being splitted into domains. We have performed an in-situ deformation experiment on such single-domained films (~100-nm-thick PbTiO<sub>3</sub> film), and found that many of these single-domained grains remain unchanged even under a high stress or equivalently a high electric field.<sup>19</sup> Therefore, the “ground state” of very thin films may be different from that of thick films or ceramics. The former, generally composed of nanometer-sized grains, has a ground state characterized by a predominant single-domained grains; the latter, composed of larger grains, has a ground state characterized by multidomained grains. This result is analogous to that in ferromagnetic films.<sup>20</sup>

Keeping the above idea in mind, one can easily understand the drastic change of coercive field ( $E_c$ ) and dielectric permittivity ( $\epsilon$ ) below a critical thickness (e.g., 200–300 nm). Below this critical thickness (or correspondingly a critical grain size ~150 nm), a domain structure transition from multidomained predominance to single-domained predominance occurs. Single-domained grains become stable and dominating. As a result, the formation of new domains (nucleation) under external field becomes much more difficult; this is equivalent to a marked increase in coercive field. Also because of the lack of domain walls in very thin films, the polarization change due to domain wall motion at low field is insignificant, consequently the associated permittivity is low. Therefore, the sharp increase in coercive field and drop in permittivity in very thin ferroelectric films can be reasonably explained in terms of the stabilization of single-domained grains at small size, as found in our experiment.

The grain-size dependence (and, equivalently, the thickness dependence) of average domain wall density determined in the present study is shown in Fig. 2. For grain size >150 nm, with the decrease of grain size, domain wall density increases due to the narrowing of domains; for grain size <150, domain structure changes from multidomain predominance to single-domain predominance, and domain wall density decreases rapidly. Figure 2 also includes a schematic grain-size dependence of  $E_c$  and  $\epsilon$ . It is clear that anomaly in  $E_c$  and  $\epsilon$  around thickness 200–300 nm (or grain size ~150 nm) corresponds very well with the domain structure transition from multidomain predominance to single-domain predominance at this size.

Some works<sup>16</sup> have shown that in ferroelectric ceramics there exists a square-root dependence of domain width  $w$  on

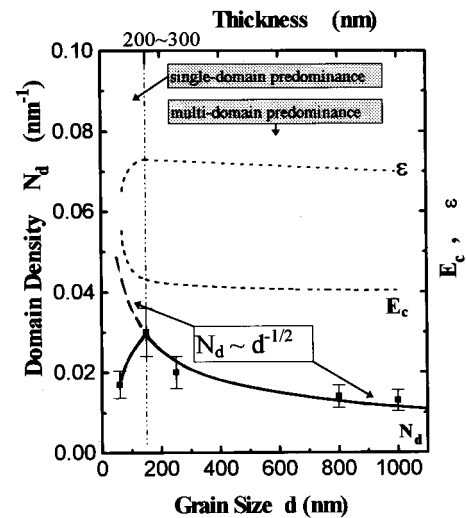


FIG. 2. Grain-size dependence of average domain wall density  $N_d$ . Schematic size dependence of coercive field ( $E_c$ ) and permittivity ( $\epsilon$ ) is also included. It can be seen that the  $N_d \sim d^{-1/2}$  relationship (as indicated) is essentially valid for  $d > 150$  nm, but not valid for  $d < 150$  nm.

grain size  $d$ , i.e.,  $w \sim d^{1/2}$ . As domain density  $N_d$  is in inverse proportion to domain width  $w$ , then it follows that  $N_d \sim d^{-1/2}$ . It is interesting to verify if this relation is valid in thin films. It is found that in our thin film samples this relation is essentially valid for grain sizes larger than 150 nm, as shown in Fig. 2. For smaller grains ( $d < 150$  nm) this relation is invalid, since in such a case we have observed that domain density drastically decreases rather than increases with decrease of grain size, in contrary to the prediction of the above relation. The invalidity of this relation below  $d \sim 150$  nm signals the change of the ground state of ferroelectric crystals at small size.

In conclusion, we have shown that in unique, free standing polycrystalline PbTiO<sub>3</sub> thin films the apparent thickness dependence of electrical properties ( $E_c$  and  $\epsilon$ ) is in fact controlled by an inherent grain-size dependence. There exists a domain structure transition from multidomain predominance to single-domain predominance at grain size ~150 nm (or, equivalently, a thickness 200–300 nm). The change of ferroelectric properties at this size can be satisfactorily explained by the corresponding domain structure change.

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