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The effect of grain size on domain structure in unsupported PbTiO₃ thin films

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Abstract. The effect of grain size on domain structure in unsupported PbTiO₃ thin films with grains (70–250 nm) was studied by using TEM. It is found that there probably exists a critical grain size near 200 nm, at which an abrupt change in domain structure occurs. Above this size, domains, which are lamellar microtwins, appear in almost all of the coarse grains. The domain width decreases with grain size. Below this size, however, most of the grains are single-domain ones, while some irregular and curved domain walls appear only in a small portion of the fine grains. The number of the single-domain grains increases with decreasing grain size. Such a grain-size dependence of domain structure is correlated with the anomalous behaviours of the coercive field E_c and dielectric constant ϵ_r in ferroelectric thin films. This interesting result has not been reported before.

There is a significant and growing interest in ferroelectric thin films, due to their potential applications in microelectronics. It is known that domains are very important features of ferroelectric materials and play a critical role in the performance of such materials. The domain structure in the sub-half-micrometre-thick ferroelectric thin films is expected to differ from that in corresponding bulk ceramics, since these thin films do not behave in exactly the same way as do their bulk ceramic counterparts. Domain structure in ferroelectric ceramics has been extensively studied [1–8]. It has been found that grain size strongly affects the domain structure and hence the electrical properties of ferroelectric ceramics. Much less is known, however, about domain structure in thin films [9–18], although it was empirically observed that domain widths become much smaller as the grain size or film thickness decreases [10, 11]. This may be due to increased strain in the thinner films, due to mismatch between substrates and films (note that the films are not free standing) [17]. Furthermore, these studies concerned mostly thicker or coarse-grained (>200 nm) films; few domain investigations for very thin or fine-grained films have been reported [11].

It was found that the dielectric constant ϵ_r of PbTiO₃ ribbon decreased abruptly at grain sizes below 200 nm rather than increasing monotonically with decreasing grain size [19]. On the other hand, it has been established empirically that the dependence of the coercive field E_c upon film thickness d becomes anomalously large below $d = 200$ nm, changing abruptly from $d^{-1/3}$ to an unexplained $d^{-4/3}$ dependence [17, 20, 21]. This change is closely and quantitatively analogous to that observed in magnetic films, in which the structure of domains changes from Bloch walls to Néel walls [22–24]. The effort to obtain a clear understanding of these abnormal behaviours of ferroelectric thin films, however, has been hampered due to a lack of detailed information on the domain structure of very thin or fine-grained (<200 nm) films. Clearly, to understand the abnormal behaviours of E_c and

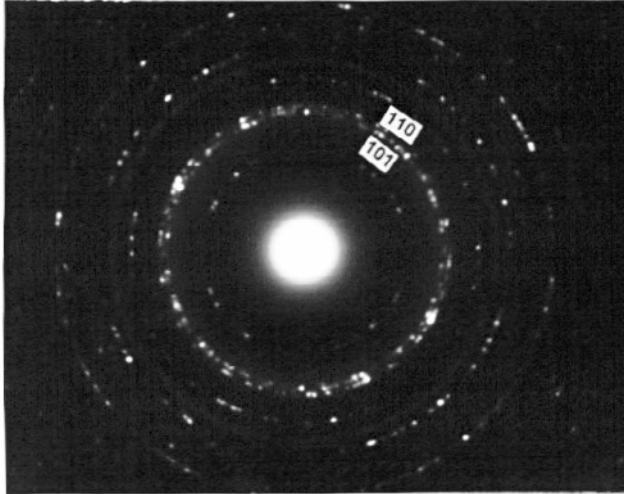


Figure 1. The SAD pattern of the four-coat thin film fired at 650 °C.

ϵ_r , it is important to study the domain structure of very thin or fine-grained (<200 nm) ferroelectric films.

In the present study the domain structure in unsupported PbTiO_3 thin films with grains (70–250 nm) is investigated by using TEM. It is observed that, at grain sizes below a critical size (about 200 nm), an increasing number of grains no longer show 90° domains. This new observation correlates with the anomalous behaviours of E_c and ϵ_r in ferroelectric thin films.

The PbTiO_3 thin films in our experiments were deposited on NaCl substrates by the sol-gel method. The detailed processing procedures have been presented previously [25, 26]. One-layer gel films were spin-coated on NaCl substrates from 0.5 M coating solution. A typical fully crystallized, single-layer film had a thickness of approximately 70 nm. Thicker films were fabricated by multiple coatings. The films were pyrolysed at 350 °C for 30 min after each coating and then annealed at 650 °C for 30 min.

The free-standing thin films were made by dissolving away NaCl substrates in water. The unsupported films were collected on copper meshes 3 mm in diameter. The one-coat films could be used for TEM investigations without further thinning. For three-coat or four-coat films, TEM specimens were prepared by ion milling. The ion milling was performed using an Ar^+ beam ($E = 5$ keV) at a small incident angle (about 7°) with respect to the specimen surfaces (in order not to disturb the domain configuration in the film). TEM experiments were carried out on a JEM-200CX operated at 200 kV.

Figure 1 shows the selected-area electron diffraction (SAD) pattern of the four-coat thin film fired at 650 °C. It can be seen that the rings (101) and (110) are clearly split (with a spacing of about 1 mm). Such splittings were observed in all other specimens as well, indicating that all specimens were of tetragonal structure. The result was also confirmed by using x-ray diffraction. We can also see from figure 1 that the film is randomly oriented polycrystalline PbTiO_3 thin film. Figure 2 shows the bright-field TEM micrographs of the thin films. Figures 2(a)–(c) show the four-coat, two-coat and one-coat films fired at 650 °C, respectively. As is shown in figure 2, all of the grains are nearly spherical and their sizes are homogenous throughout any particular film. Grains become rapidly smaller as the thickness

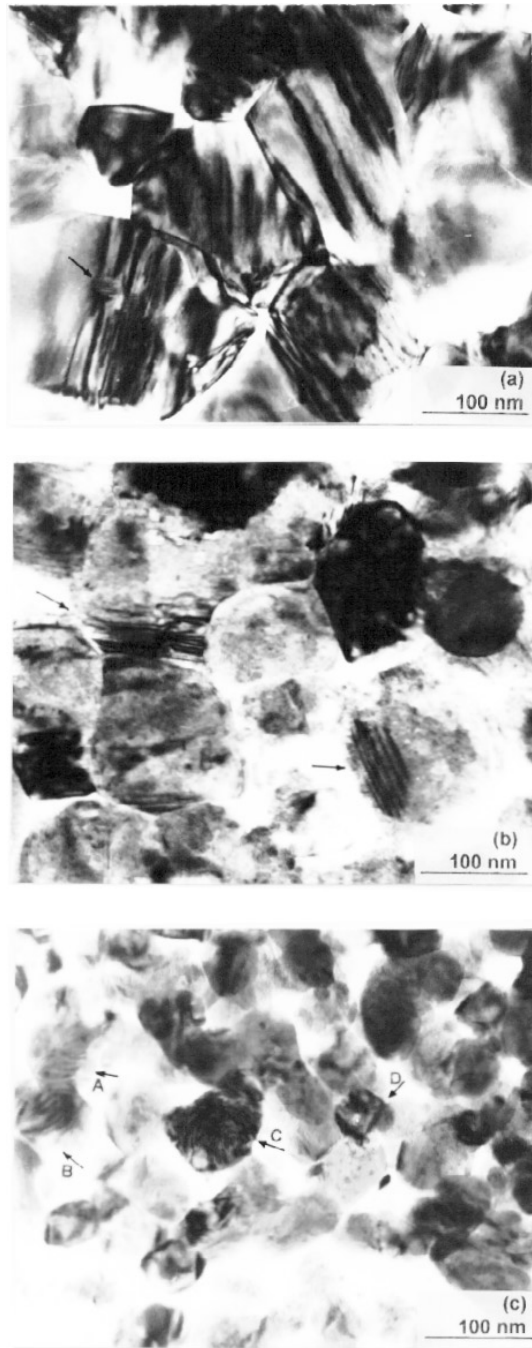


Figure 2. TEM micrographs of the (a) four-coat, (b) two-coat and (c) one-coat films fired at 650°C .

of the films decreases. The grains are not fully and closely clamped, especially in the thinner films. Such microstructural instability and discontinuity were also observed by Seifert *et al*

in very thin (about 80 nm) PbTiO_3 films [27]. Nevertheless, further examination reveals that not all of the bright regions are micropores and in most cases they are only very thin amorphous layers among the grains. Embedded pores in grains as described in the literature [13–15] were not found in our films.

The film in figure 2(a) has a grain size range of 200–250 nm. Domains are present in almost all of the grains in the film and their structure is similar to that in bulk ceramics, whereas only a few small grains are single-domain ones (without 90° -domain walls). The domain walls usually terminate at the grain boundaries. The domain width was measured to be 10–40 nm, which is consistent with that observed in coarse-grained (0.2–0.55 mm) PbTiO_3 thin films (10–55 nm) [12] and much less than that observed in bulk PZT ceramics ($\geq 0.1 \mu\text{m}$) [4]. It was also noted that the fine fringes as indicated by arrows are ripples caused by double diffraction of an electron beam rather than ‘sub-domains’. However, when the grain size decreases to 120–180 nm with film thickness, as shown in figure 2(b), no domains are seen in most of the grains in the fine-grained film and only a few grains exhibit lamellar domains as indicated by arrows. The domain width is in the range 5–20 nm, which is less than that observed in figure 2(a). As the grain size further decreases (70–90 nm), as shown in figure 2(c), the typical lamellar domain is rarely seen. Instead, in a few grains domain walls are often curved (such as the grains A and B) and irregular (for example the grain C), while almost all of the grains are single domain. In TEM, the bending of domain walls has also been observed by many investigators [28, 29]. Tsai *et al* have suggested that the domain walls can be bent due to the distribution of the strain field, the interactions among the domain walls or the charging of domain walls [29].

It was also observed that the smaller the grains the higher the percentage of single-domain grains, even in the same film. Specimen-tilting experiments have confirmed that the above observation is not a contrast effect. From TEM contrast we can deduce that almost all of the domain walls observed are 90° walls in the thin films. 180° walls are rarely seen.

For coarse-grained (>200 nm) thin films, it has been found by many investigators [11–16] that domains, which are lamellar microtwins, appear in almost all the grains. The domain width decreases with grain size. Combining our results above for the films with grains (70–250 nm), the conclusion can be drawn that there probably exists a critical grain size near 200 nm, at which an abrupt change in domain structure occurs. Below this size, strain can be released at grain boundaries during ferroelectric phase transformations and most grains are single-domain ones, whereas irregular and curved domain walls appear only in a small portion of the fine grains. The number of the single-domain grains increases with decreasing grain size. This interesting observation has not been reported before. Such a grain-size effect on domain structure also exists in ferroelectric ceramics. Arlt *et al* [5] observed that, at grain sizes below $0.7 \mu\text{m}$, an increasing number of grains no longer exhibit 90° domains in BaTiO_3 ceramics. It is thus suggested that the changes in domain structure observed in our films are originally due to grain-size dependence rather than film-thickness dependence.

Clearly, the micropores in the films may reduce the constraint force among the grains and promote the formation of single-domain grains. However, further examinations indicate that this may be only a secondary effect to grain size. In figure 2(c), for example, the grain C should be single domain from the role of micropores, but domains appear clearly in it due to its larger grain size. On the other hand, the smaller grain D is a single-domain one even though it is fully clamped by its surroundings.

Additionally, the above conclusion has been confirmed by our XRD results which will be presented in another paper. Coincidentally, Nakamura *et al* [19] found that the dielectric

constant of PbTiO₃ ribbon decreased abruptly at grain sizes below 200 nm rather than increasing monotonically with decreasing grain size. It has been suggested that in addition to the intrinsic dielectric constant, the contribution of 90°-domain walls to dielectric constant is proportional to the total area of 90°-domain walls per unit volume [5]. Above 200 nm, the 90°-domain wall density increases with decreasing grain size as stated above. Thus the contribution of domain walls to the dielectric constant also increases. The surprising decrease in ϵ_r observed at grain size below 200 nm correlates to the abrupt absence of domain walls.

The abnormally large coercive field at film thickness below 200 nm is likely to be related to the abrupt presence of a large number of single-domain grains below a critical grain size (such as 200 nm), since film thickness has a one-to-one correspondence to grain size under the same processing conditions [30]. We also investigated the dynamic behaviour of domain walls in the fine-grained films and the results suggested that the coercive fields of the single-domain grains would be really very large [31].

In summary, an effort has been made to study the effect of grain size on domain structure in sol-gel-deposited PbTiO₃ thin films. It is found that the domain structure in the fine-grained (<200 nm) thin films is quite different from that in the coarse-grained (>200 nm) thin films. Such a grain-size dependence of domain structure correlates to the abnormal behaviours of E_c and ϵ_r in ferroelectric thin films.

Acknowledgment

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