

**First principles study on ferroelectricity of
PbTiO₃ nanofilms with internal structures**

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Chapter 1 Introduction

1.1 Ferroelectricity and polarization pattern in ferroelectric nanofilms

Ferroelectric materials have attracted much great interest owing to their prominent electric property. Ferroelectricity [1-3] is defined as a property that materials exhibit non-vanishing spontaneous polarization, which is a dipole moment per unit volume, even in the absence of external electric fields. By utilizing this property, ferroelectric materials have been widely applied to technological devices such as ferroelectric random access memories (FeRAM), actuators, sensors and transducers [4-8].

Among of some ferroelectric materials such as perovskite oxide type [9], hydrogen bonded type, organic type, and so on, the perovskite oxide is particularly well used for technological devices owing to the outstanding polarization property. Figure 1.1 shows the lattice structures of perovskite oxides ABO_3 in the paraelectric (PE) and ferroelectric (FE) phases. The structures may be viewed as consisting of BO_6 octahedra surrounded by A ions. In the PE phase with a cubic unit cell structure (Fig. 1.1(a)), there is no polarization because of the centro-symmetrical structure. In the FE

phase with a tetragonal unit cell structure (Fig. 1.1(b)), the B and O ions inside BO_6 octahedra shift relative to the A ions, and the spontaneous polarization emerges due to the non-symmetrical structure. The FE phase is generally stable than PE phase energetically below the critical temperature called Curie point, and it has two equivalent states with $\mathbf{P}_{\text{UP}}$ and $\mathbf{P}_{\text{DOWN}}$ spontaneous polarization.

Since spontaneous polarization arises from the distorted atomic structure, ferroelectricity is much sensitive to the applied stress or strain that changes the distortions [10-14]. For a bulk ferroelectric perovskite oxide, the ferroelectric polarization is enhanced due to the tension along the polar axis, because the tetragonal distortion of the perovskite lattice is increased, while the polarization is decreased under compression [15-16]. The coupling effect between the mechanical deformation and electric properties is known as a “multi-physics property”.

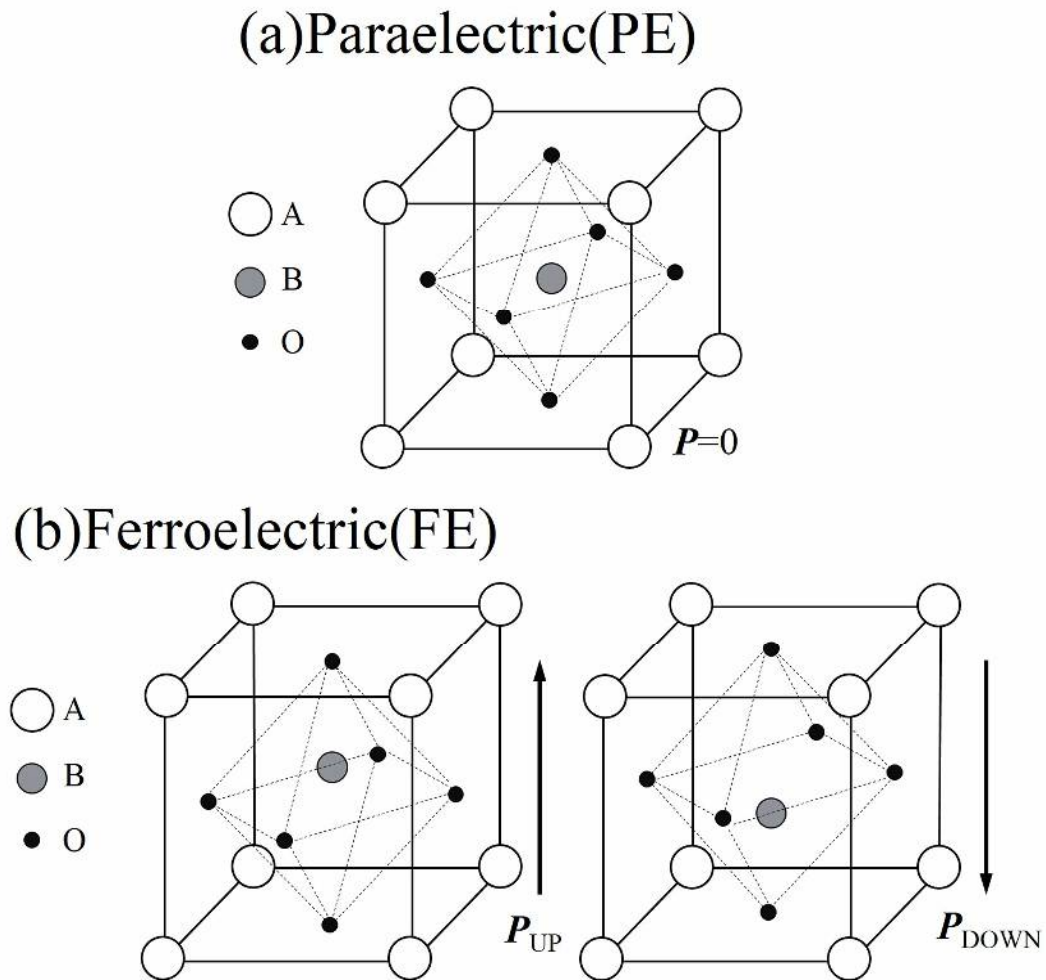


Fig.1.1 Lattice structures of perovskite oxides ABO_3 . (a) Paraelectric (PE) phase that there is no polarization due to the centro-symmetrical structure. (b) Ferroelectric (FE) phase with upward and downward polarization, P_{UP} and P_{DOWN} , respectively, due to the non-symmetrical structure.

Throughout the whole crystal of the ferroelectric perovskite oxides, the spontaneous polarization is usually not uniformly aligned along the same direction [17]. Figure 1.2 shows the schematic illustration of the crystal structure of ferroelectric perovskite oxide in the monodomain and polydomain phase. In the monodomain phase, the polarization pattern is single (Fig. 1.2 (a)). On the other hand, in the polydomain phase, the crystal structure consists of domains [20], each of which has a uniformly oriented spontaneous polarization, so that the polarization pattern is random throughout the whole crystal (Fig. 1.2(b)). It is generally known that the polarization perpendicular to the surface emerges the depolarizing field [18-19], and the field destabilizes ferroelectricity. In the polydomain phase, the random polarization pattern leads to the zero net polarization and stabilizes the ferroelectric state. Thus, the polarization pattern in the crystal structure is significantly important for the ferroelectric properties of ferroelectric perovskite oxides.

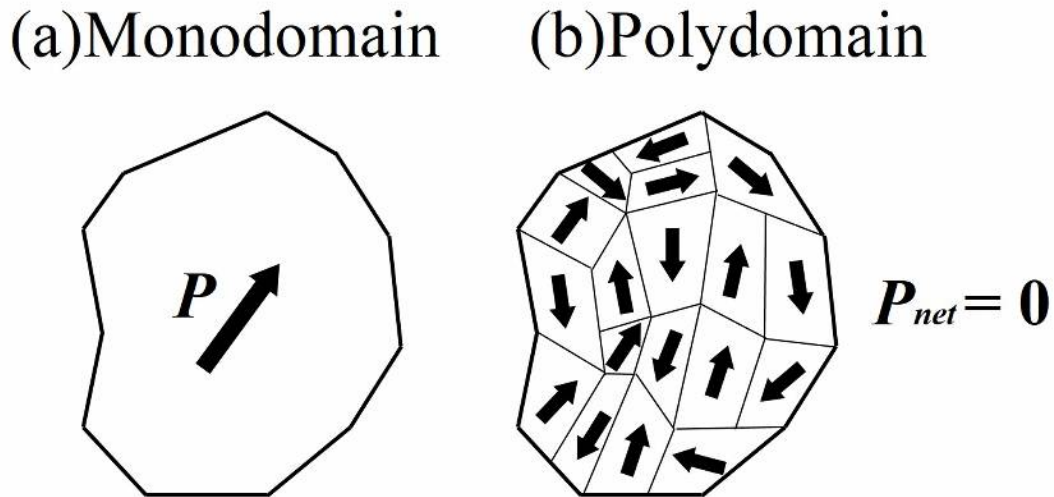


Fig.1.2 Schematic illustration of the crystal structure of ferroelectric perovskite oxide in the (a) monodomain and (b) polydomain phase. In the monodomain phase, the polarization pattern is single. In the polydomain phase, the crystal structure consists of domains, each of which has a uniformly oriented spontaneous polarization, so that the polarization pattern is random throughout the whole crystal. This random polarization pattern is generally important for the stability of ferroelectric perovskite oxides.

In recent years, due to the demand for device miniaturization, significant developments in manufacturing technology have enabled us to obtain ferroelectric nanomaterials such as nanofilm [21-23], nanowire [24-27], nanotube [28-30], nanoparticle [31-33]. Among of them, nanofilm is the most widely applied for ferroelectric devices. Ferroelectric property in nanofilm is strongly affected by even a slight atomic displacement, since the spontaneous polarization in ferroelectric perovskite oxide is derived from the atomic distortion. So that, for the materials design and reliability of ferroelectric nanofilm, the precise investigation from the atomistic and electronic points of view is extremely important.

As a surface of ferroelectric nanofilm, there are some types of surface termination such as (001), (011) and (111). Analytical study have revealed that (001) surface is the most energetically stable in most perovskite oxide such as PbTiO_3 , BaTiO_3 , SrTiO_3 and CaTiO_3 [34-37]. So that, we investigate the ferroelectric nanofilms with (001) surface due to the academic importance.

Owing to the recent experimental investigation of ferroelectric nanofilms, some “surface structure” such as flat surface, surface step

[38-41], island [42-45] have been found in ferroelectric nanofilm. The “surface structure” strongly affects the polarization pattern, because the coordination number decreases more drastically than bulk and the atomic and electronic structure is disarranged. For example, in nanofilm with polarization parallel to the (001) surface, gradually enhanced polarization pattern as it come close to PbO(001) surface is appeared, on the other hand, the polarization is decreased as it come close to TiO₂(001) surface [46]. Additionally, since the ratio of the “surface structure” with respect to the entire volume is significantly large, the ferroelectric properties of ferroelectric perovskite nanofilms is strongly affected by the “surface structure”. Hence, to investigate the effect of “surface structure” for the polarization pattern is significantly important for understanding of ferroelectric properties of ferroelectric nanofilms.

A flat surface is one of the simplest “surface structure” of nanofilms. As above mentioned, at the flat (001) surface with polarization parallel to the surface where the coordination number is decreased, gradually enhanced and decreased polarization pattern is appeared depending on the surface termination layer. On the other hand, at the flat (001) surface with

polarization perpendicular to surface, not only the coordination number is decreased, but also the polarization surface charge is induced at surface. Fong et.al have experimentally investigated that the ferroelectric PbTiO_3 nanofilm with above 1.2 nm thickness on the SrTiO_3 forms polydomain structures, where polarization direction changes from upward to downward across the domain wall, for screening the depolarizing field [47]. However, the polarization pattern of the nanofilm with below 1.2nm thickness, where the surface-surface distance is ultimately close, is not cleared. So that we need investigate it for further device miniaturization.

Surface step on the (001) surface of perovskite type oxide is often observed by atomic force microscopy. The surface step characteristically possesses an atomically sharp edge structure consisting of (100) and (001) surfaces [40,48-50]. Hence, the coordination number at surface step changes more drastically than flat (001) surface, and the atomic and electronic structure are disarranged dynamically. So that, it is necessary to reveal the effect of surface step for the polarization pattern. Against the surface step consisting of (100) and (001) flat surface in the nanofilm, there are three typical polarization directions, [100], [010] and [001] directions.

First of all, we investigate the surface step with polarization along [010] direction, because this situation is the most simple for understanding the effect of coordination number due to no surface polarization charge. Incidentally, the ferroelectricity at the surface step with polarization along [100] direction has been investigated by our colleague Wang et.al. [51].

On the other hand, the “internal structure” such as vacancy [52-57], impurity [58], grain-boundary [59-61], domain-wall [62-63], also strongly affect the ferroelectricity of nano-films because of their distorted arrangement of atomic positions. For the more detailed understanding of ferroelectricity in nanofilm, it is essential to investigate the effect of “internal structure” as well as “surface structure”.

Oxygen vacancy is the common internal structure, and it has a lot of attention because of the strong effect for the material properties [64-71]. Shimada et.al have investigated the oxygen-vacancy in bulk and in surface, and found the emergence of ferromagnetism in non-magnetic PbTiO_3 [72-74]. As mentioned above, nanofilms with polarization perpendicular to the surface has polydomain structure. So that, we need to study the relationship among surface, domain wall and vacancy for understanding the

complex situation in ferroelectric polydomain nanofilm with oxygen-vacancy. Therefore, first of all, we need to investigate the ferroelectricity in domain wall with oxygen-vacancy to understand the complex situation in nanofilm step-by-step.

1.2 Atomic simulations for investigating ferroelectric nanofilms

So far, as a method of investigating the electronic properties of ferroelectric nanomaterials, the experimental and simulation method have been used. By using experimental method, the polarization pattern in nanomaterials, and the change of ferroelectricity against the mechanical strain and external electric field have been investigated. However, in experimental method, it is difficult to observe the detailed atomic and electronic structure and slight change in spontaneous polarization due to the limitation of magnification in microscope, and to investigate the polarization pattern in ultimate small nanomaterials due to the hardship of sample preparation. So that, the simulation method becomes an important tool for the investigation on ferroelectric nanofilms.

Ab initio (first-principles) calculations based on the density functional theory (DFT) [75,76] are the most accurate method for investigating the detailed atomic and electronic structure. In first-principles calculations, the electronic state which determines the interaction among atoms is analyzed by self-consistently solving the Schrödinger equation within the

one-electron approximation, namely, Kohn-Sham equation. Recently, the first-principles calculation has also been used to investigate the ferroelectrics, and it has successfully predicted various kinds of properties, e.g., crystal structures [77-79], electronic states [80,81], and the origin of ferroelectricity [82].

Moreover, a precise formula which describes the spontaneous polarization under periodic boundary conditions is recently derived on the basis of the Berry phase theory [83], which promotes the fundamental studies on ferroelectric properties in the perovskite oxides. So that, this simulation method has been extended to complex system, such as surfaces [84-87], domain walls [88-90], grain boundaries [91-94], nanowires [95-99], nanotubes [100,101], vacancies [102,103] and impurities [104] which revealed that first-principles calculations can precisely describe the atomic and electronic structures. Thus, we employ the first-principles calculation in this thesis to investigate the polarization pattern and atomic structure in ferroelectric nanofilms.

1.3 Overview of this thesis

In this thesis, I aim to study the effect of “surface structure” and “internal structure” for the polarization pattern in the ferroelectric perovskite nanofilms by means of first-principles density functional theory calculations.

In Chapter 2, the polarization pattern in PbTiO_3 nanofilms with below 1.2nm thickness, which has the flat (001) surface with polarization perpendicular to surface. And, the detailed atomic and electronic structures are also discussed.

In Chapter 3, the ferroelectricity and atomic and electronic structure in PbTiO_3 surface steps consisting of (100) and (001) surfaces are studied. Moreover, the effect of in-plane strain for the polarization pattern is also investigated.

In Chapter 4, as the first step for the future challenges to reveal the complex effect between “surface structure” and “internal structure” in ferroelectric nanofilms, the polarization pattern at the oxygen vacancy in domain wall.

Finally, conclusions of this thesis is presented in Chapter 5.

References

- [1] F. Jona and G. Shirane, *Ferroelectric Crystals*, Dover, New York (1993).
- [2] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon, Oxford (1977).
- [3] M. Tokunaga, *Dielectrics* (in Japanese), Baifukan, Tokyo (1991).
- [4] J. F. Scott, *Ferroelectric Memories*, Springer, Berlin (2000).
- [5] R. Ramesh, *Thin Film Ferroelectric Materials and Devices*, Kluwer Academic, Boston (1997).
- [6] T. Ikeda, *Fundamentals of piezoelectricity*, Oxford University Press, New York (1996).
- [7] K. Uchino, *Piezoelectric and electrostrictive actuators: From fundamentals to applications* (in Japanese), Morikita Publisher, Tokyo (1986).
- [8] T. Shiosaki, *Piezoelectric Materials and Applications* (in Japanese), CMC Publisher, Tokyo (1987).
- [9] The Society of Materials Science, Japan, *Ferroelectricity and high-T_c superconductivity in the perovskite-type materials* (in Japanese),

Shoukabou, Tokyo (1993).

[10] Z. Wu and R. E. Cohen, Physic Review Letters, **95**, 037601 (2005).

[11] Y. Duan, L. Zin, G. Tang and C. Chen, Journal of Applied Physics, **105**, 033706 (2009).

[12] Y. Umeno, T. Shimada, T. Kitamura and C. Elsässer, Physical Review, **74**, 174111 (2006).

[13] D. G. Schlom, L-Q. Chen, C-B. Eom, K. M. Rabe, S. K. Streiffer and J-M Triscone, Annual Review of Materials Research, 37, 589 (2007).

[14] T. Shimada and T. Kitamura, Mechanical Engineering Reviews, 1, 2 (2014).

[15] I. Kornev, L. Bellaich, P. Bouvier, P. -E. Janolin, B. Dkhil and J. Kresel, Physical Review Letters, **95**, 196804 (2005).

[16] O. Dieguez, K. M. Rabe and D. Vanderbilt, Physical Review B, **72**, 144101 (2005).

[17] D. Damjanovic, Reports on Progress in Physics, 61, 1267 (1998).

[18] I. P. Batra and B. B. Silverman, Solid State Commun, 11, 291 (1972).

[19] R. R. Mehta, B. D. Silverman and J. T. Jacobs, Journal of Applied Physics, 44, 3379 (1973).

-
- [20] C. Kittel, *Physical Review*, **70**, 965 (1946).
- [21] K. Wasa, Y. Haneda, T. Sato, H. Adachi and K. Setsune, *Vacuum*, **51**, 591 (1998).
- [22] H. Fujisawa, M. Shimizu, H. Niu, H. Nonomura and K. Honda, *Applied Physics Letters*, **86**, 012903 (2005).
- [23] T. Suzuki, Y. Nishi and M. Fujimoto, *Philosophical Magazine A*, **79**, 2461 (1999).
- [24] Z. Ren, G. Xu, Y. Liu, X. Wei, Y. Chu, X. Zhang, G. Lv, Y. Wang, Y. Zeng, P. Du, W. Weng, G. Shen, J. Z. Jiang and G. Han, *Journal of American Chemical Society*, **132**, 5572 (2010).
- [25] H. Gu, Y. Hu, J. You, Z. Hu, Y. Yuan and T. Zhang, *Journal of Applied Physics*, **101**, 024319 (2007).
- [26] W. S. Yun, J. J. Urban, Q. Gu and H. Park, *Nano Letters*, **2**, 447 (2002).
- [27] X. Lu, D. Zhang, Q. Zhao, C. Wang, W. Zhang and Y. Wei, *Macrometer Rapid Councinations*, **27**, 76 (2006).
- [28] Y. Yang, X. Wang, C. Sun and L. Li, *Journal of American ceramic society*, **91**, 3820 (2008).

-
- [29] J. Kim, S. A. Yang, Y. C. Chol, J. K. Han, K. O. Jeong, Y. J. Yun, D. J. Kim, S. M. Yang, D. Yoon, H. Cheong, K-S. Chang, T. W. Noh and S. D. Bu, *Nano Letters*, 8, 1813 (2008).
- [30] C. Bae, H. Yoo, S. Kim, K. Lee, J. Kim, M. M. Sung and H. Shin, *Chemistry of Materials*, 20, 756 (2008).
- [31] M. Leong, D. J. Bayrel, J. Shi and X. Wang, *Science of Advanced Materials*, 4, 832 (2012).
- [32] V. Domenici, B. Zupancic, V. V. Laguta, A. G. Belous, O. I. V'yunov, M. Remskar and B. Zalar, *The Journal of Physical Chemistry C*, 114, 10782 (2010).
- [33] J. Q. Qi, Y. Wang, W. P. Chen, L. T. Li and H. L. W. Chan, *Journal of Nanoparticle Research*, 8, 959 (2006).
- [34] J-M. Zhang, Q. Ping, K-W. Xu and V. Ji, *Computational Materials Science*, 44, 1360 (2009).
- [35] G-X. Zhang, Y. Zie, H-T, Yu and H-G Fu, *Journal of Computational Chemistry*, 30, 1785 (2009).
- [36] R. I. Eglitis, *International Journal of Modern Physics B*, 28, 143009 (2014).

- [37] Q. Pang, J-M. Zhang, K-W. Xu and V. Ji, *Applied Surface Science*, **255**, 8145 (2009).
- [38] Cho G B, Yamamoto M and Endo Y, *Thin Solid Films*, **464**, 80 (2004).
- [39] Takahashi K, Suzuki M, Yoshimoto M and Funakubo H, *Japanese Journal of Applied Physics*, **45**, L138 (2006).
- [40] Y. Yamashita, K. Mukai, J. Yoshinobu, M. Lippmaa, T. Kinoshita and M. Kawasaki, *Surface Science*, **514**, 54 (2002).
- [41] J. L. Blok, *Experimental design of oxide materials* (2015).
- [42] Y. Kim, H. Han, Y. Kim, W. Lee, M. Alexe, S. Baik and J. K. Kim, *Nano Lett*, **10**, 2141 (2010).
- [43] A. Schilling, D. Byrne, G. Catalan, K. G. Webber, Y. A. Genenko, G. S. Wu, J. F. Scott and J. M. Gregg, *Nano Lett*, **9**, 3359 (2009).
- [44] J. Varghese, T. Ghoshal, N. Deepak, C. O'Regan, R. W. Whatmore, M. A. Morris and J. D. Holmes, *Chemistry of Materials*, **25**, 1458 (2013).
- [45] J. Li, M. Luo, W. Weng, K. Cheng, P. Du, G. Shen, G. Han, *Applied Surface Science*, **256**, 342 (2009).
- [46] Y. Umeno, T. Shimada, T. Kitamura and C. Elsässer, *Physical Review B*, **74**, 174111 (2006).

- [47] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, C. Thompson, *Science*, **304**, 1650 (2004).
- [48] E. A. Kotomin, E. Heifets, S. Dorfman, D. Fuks, A. Gordon and J. Maier, *Surface Science*, **566**, 231 (2004).
- [49] M. W. Chu, I. Szafraniak, R. Scholz, C. Harnagea, D. Hesse, M. Alexe and U. Gosele, *Nature Materials*, **3**, 87 (2004).
- [50] J. H. Jeon and S. K. Choi, *Applied Physics Letters*, **91**, 091916 (2007).
- [51] X. Wang, Doctoral thesis at Kyoto university, section 2.
- [52] W. L. Warren, H. N. Al-Shareef, D. Dimos, B. A. Tuttle and G. E. Pike, *Applied Physics Letters*, **68**, 12 (1996).
- [53] W. L. Warren, D. Dimos and R. M. Waser, *MRS Bulletin*, **21**, 7 (1996).
- [54] J. F. Scott and M. Dawber, *Applied Physics Letters*, **76**, 25 (2000).
- [55] L. He and D. Vanderbilt, *Physical Review B*, **68**, 134013 (2003).
- [56] X. Du and I. W. J. Chen, *Journal of Applied Physics*, **83**, 7789 (1998).
- [57] C. H. Park and D. J. Chadi, *Physical Review B*, **57**, 22 (1998).
- [58] Y. Wang and C. Nan, *Applied Physics Letters*, **89**, 052903 (2006).
- [59] S. Hutt, S. Kastleier and C. Elsasser, *Jornal of Physics Condensed Matter*, **13**, 3949 (2001).

-
- [60] W. T. Geng, Y. J. Zhao and A. J. Freeman, *Physical Review B*, **63**, 060101 (2000).
- [61] S. -D. Mo, W. Y. Ching, M. F. Chisholm and G. Duscher, *Physical Review B*, **63**, 060101 (2000).
- [62] S. O. Hruszkewycz, M. J. Highland, M. V. Holt, D. Kim, C. M. Folkman, C. Thompson, A. Tripathi, G. B. Stephenson, S. Hong and P. H. Fuoss, *Physical Review Letters*, **110**, 177601 (2013).
- [63] J. K. Shang and X. Tan, *Acta Materialia*, **49**, 2993 (2001).
- [64] W. L. Warren, D. Dimos and R. M. Waser, *MRS Bull.* **21** 40 (1996).
- [65] J. F. Scott and M. Dawber, *Applied Physics Letters* **76** 3801 (2000).
- [66] W. L. Warren, H. N. Al-Shareef, D. Dimos, B. A. Tuttle and G. E. Pike, *Applied Physics Letters* **68** 1681 (1996).
- [67] S. Pöykkö S and D. J. Chadi, *Physical Review Letters* **83** 1231 (1999).
- [68] L. He and D. Vanderbilt, *Physical Review B* **68** 134103 (2003).
- [69] X. Du and I. Wei Chen, *Journal of Applied Physics* **83** 7789 (1998).
- [70] G. Burns and B. A. Scott, *Physical Review Letters* **25** 1191 (1970).
- [71] X. Du and I. W. Chen, *Journal of Applied Physics* **83** 7789 (1998).
- [72] T. Shimada, Y. Uratani and T. Kitamura, *Acta Materialia*, **60**, 6322

(2012).

[73] T. Shimada, Y. Uratani and T. Kitamura, *Applied Physics Letters*, **100**, 162901 (2012).

[74] T. Shimada, T. Ueda and T. Kitamura, *Physical Review B*, **87**, 174111 (2003).

[75] P. Hohenberg and W. Kohn, *Physical Review*, **136**, B864 (1964).

[76] W. Kohn and L. Sham, *Physical Review*, **140**, A1133 (1965).

[77] R. E. Cohen and H. Kraukauer, *Physical Review B*, **42**, 6416 (1990).

[78] R. D. King-Smith and D. Vanderbilt, *Physical Review B*, **49**, 5828 (1994).

[79] W. Zhong and D. Vanderbilt, *Physical Review Letters*, **74**, 2587 (1995).

[80] M. Posternak, R. Resta and A. Baldereschi, *Physical Review B*, **50**, 8911R (1994).

[81] P. Ghosez, X. Gonze, P. Lambin, J. –P. Michenaud, *Physical Review B*, **51**, 6765R (1995).

[82] R. E. Cohen, *Nature*, **358**, 136 (1992).

[83] R. Resta, M. Posternak and A. Baldereschi, *Physical Review Letters*,

70, 1010 (1993).

[84] C. Bungaro and K. M. Rabe, *Physical Review B*, **71**, 035420 (2005).

[85] B. Meyer, J. Padilla and D. Vanderbilt, *Faraday Discussion*, **114**, 395 (1999).

[86] M. Fechner, S. Ostanin and I. Mertig, *Physical Review B*, **77**, 094112 (2008).

[87] D. V. Truong, N. T. Hung, T. Shimada and T. Kitamura, *Surface Science*, **606**, 1331 (2012).

[88] B. Meyer and D. Vanderbilt, *Physical Review B*, **65**, 104111 (2002).

[89] S. Pöykkö and D. J. Chadi, *Applied Physics Letters*, **75**, 2830 (1999).

[90] T. Shimada, Y. Umeno and T. Kitamura, *Physical Review B*, **77**, 094105 (2008).

[91] W. T. Geng, Y. J. Zhao and A. J. Freeman, *Physical Review B*, **63**, 060101 (2000).

[92] S. -D. Mo, W. Y. Ching, M. F. Chisholm and G. Duscher, *Physical Review B*, **60**, 2416 (1999).

[93] P. Marton, T. Shimada, T. Kitamura and C. Elsaesser, *Physical Review B*, **83**, 064110 (2011).

- [94] T. Shimada, X. Wang, S. Tomoda, P. Mavel, C. Elsaesser and T. Kitamura, *Physical Review B*, 83, 094121 (2011).
- [95] J. W. Hong, G. Catalan, D. N. Fong, E. Artacho and J. F. Scott, *Physical Review B*, 81, 172101 (2010).
- [96] G. Pilania and R. Ramprasad, *Physical Review B*, 82, 155442 (2010).
- [97] M. Q. Cai, Y. Zheng, B. Wang and G. W. Yang, *Physical Review Letters*, 95, 232901 (2009).
- [98] G. Pilania and R. Ramprasad, *Journal of Materials Science*, 47, 7580 (2012).
- [99] T. Shimada, S. Tomoda and T. Kitamura, *Physical Review B*, 79, 024102 (2009).
- [100] T. Shimada, X. Wang, Y. Kondo and T. Kitamura, *Physical Review Letters*, 108, 067601 (2012).
- [101] J. Wang, T. Xu, T. Shimada, X. Wang, T. Y. Zhang and T. Kitamura, *Physical Review B*, 89, 144102 (2014).
- [102] T. Shimada, J. Wang, T. Ueda, Y. Uratani, K. Arisue, M. Mrovec, C. Elsasser and T. Kitamura, *Nano Lett*, 15, 27 (2015).
- [103] Z. Zhang, P. Wu, L. Lu and C. Shu, *Applied Physics Letters*, **88**,

142902 (2006).

[104] J. W. Bennett, I. Grinberg and A. M. Rappe, Journal of American Chemical Society, 130, 17049 (2008).

Chapter 2 Ferroelectricity in ultrathin polydomain PbTiO₃ films

2.1 Introduction

Ferroelectric ultrathin films have received remarkable attention because of the strong request for the miniaturization of devices such as non-volatile ferroelectric random access memory [1]. Shimada et.al indicated that, in the flat (001) surface with polarization parallel to the surface, gradually enhanced and decreased polarization pattern is appeared depending on the surface termination layer. On the other hand, at the flat (001) surface with polarization perpendicular to surface, not only the coordination number is decreased, but also the polarization surface charge which leads to the depolarizing field [2,3] is induced at surface. The depolarizing field [4] derived from the surface polarization charge suppresses ferroelectricity. Fong et.al have experimentally investigated that the ferroelectric PbTiO₃ nanofilms with above 1.2 nm thickness on the SrTiO₃ forms polydomain [5] structures, where polarization direction changes from upward to downward across the domain wall, for screening the depolarizing field. However, the polarization pattern of the nanofilm with below 1.2nm

thickness, where the surface-surface distance is ultimately close, is not cleared. So that, we need investigate it for further device miniaturization.

In this chapter, we investigated the ferroelectricity in PbTiO_3 nanofilms with (001) flat surface using ab initio density-functional theory calculations. And the detailed atomic and electronic structures of polydomain structure also discussed.

2.2 Simulation procedure

Ab initio calculations based on the density-functional theory [6,7] are conducted using the Vienna Ab initio Simulation Package (VASP) [8,9]. The electronic wave functions are expanded in-plane waves up to a cutoff energy of 500 eV. The pseudopotentials [10,11] based on the projector augmented wave (PAW) method explicitly include the O 2s and 2p, the Ti 3s, 3p, 3d and 4s, and the Pb 5d, 6s and 6p electrons in the valence states. The local-density approximation (LDA) of the Ceperley-Alder form [12] is employed to evaluate the exchange-correlation energy.

We investigate the free-standing polydomain PbTiO_3 ultrathin films with upward and downward spontaneous polarizations normal to the (001) surface. Figure 2.1 shows the simulation model of a three unit-cell thick (m

= 3) film with a domain period of six unit cells ($N_x = 6$), where m and N_x denote the number of perovskite unit cells in the film thickness and the domain period, respectively. The films with a thickness of less than or equal to three unit cells ($m \leq 3$) were simulated in this study because the existence of a polydomain ferroelectric phase has already been observed experimentally in thicker films [4]. To study the ferroelectric stability with respect to the domain period, the models with different N_x were considered, as well. The TiO_2 termination was selected for the (001) surfaces of films because the termination is energetically favorable compared to another choice of the PbO termination [13]. Twinning on both the TiO_2 (Ti centered) and PbO (Pb centered) (010) planes was considered for the 180° domain wall (see Figs .2.1(a) and 2.1(b), respectively). Since the three-dimensional periodic boundary condition was applied in the plane-wave pseudopotential calculations, a vacuum region of $l_v = 20 \text{ \AA}$ was introduced in the z direction so that undesirable interactions from the neighboring films were sufficiently avoided. Thus, the simulation cell dimensions in the x , y , and z directions were set to $N_x a$, a , and $mc + l_v$, respectively, where a and c are the theoretical lattice constants of the bulk,

$a = 3.867 \text{ \AA}$ and $c = 4.034 \text{ \AA}$ ($c/a = 1.043$). The Brillouin zone integrations were carried out using a $12/N_x \times 6 \times 2$ Monkhorst-Pack k-point mesh with a Gaussian smearing of 0.20 eV, except for $N_x = 8$ where a $2 \times 6 \times 2$ k-point mesh was used.

To obtain the equilibrated structure of the models, the atomic positions were fully relaxed using the conjugate-gradient method until all the Hellmann-Feynman forces were less than $2.5 \times 10^{-3} \text{ eV/\AA}$. The symmetry of inversion center in the domain walls was kept during the relaxation process.

Note that, because the net dipole moments in the simulation cell was completely cancelled out to be zero due to equivalent upward and downward spontaneous polarizations in the ferroelectric polydomain films, the periodic boundary condition produces no artificial external electric field, which would otherwise emerge in a single-domain film with a polarization perpendicular to its surface.

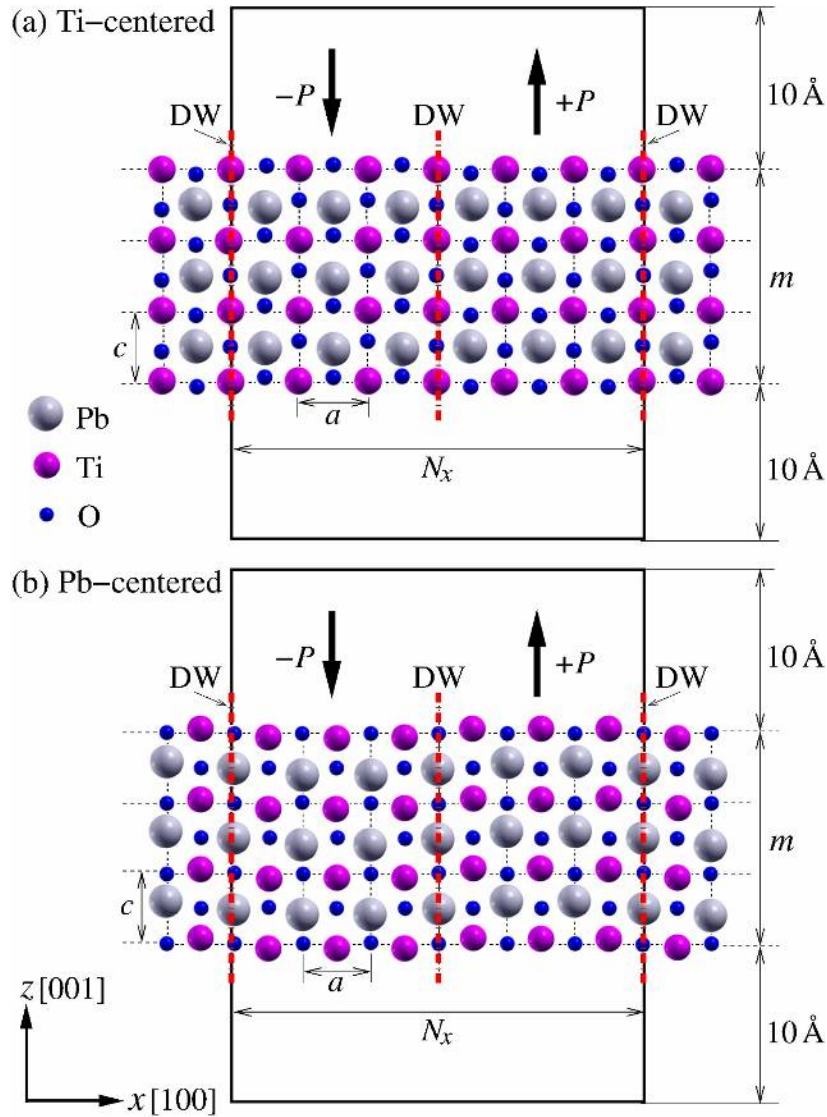


Fig.2.1 Simulation models of the free-standing PbTiO_3 ultrathin films with the TiO_2 -terminated (001) surfaces for the (a) Ti-centered and (b) Pb-centered 180° domain wall (DW) configurations. Spontaneous polarization, P , is initially set along the $+z$ and $-z$ directions on the right and left sides of the film, respectively. N_x and m denote the number of perovskite unit cells for the domain period and the thickness of film, respectively. The model shown here is $N_x = 6$ and $m = 3$. The solid boxes represent the simulation supercells.

2.3 Results and discussion

2.3.1 Stability of ferroelectric polydomain phase in ultrathin PbTiO_3 films

Figure 2.2 shows the total energy difference between the ferroelectric polydomain and paraelectric phase, ΔE , as a function of the domain period, N_x , for films with thicknesses of 3, 2, and 1 unit cells. Here, the total energy difference was divided by N_x for a fair comparison among the different domain periods. In both the Pb- and Ti-centered three unit-cell thick films ($m = 3$), the energy difference decreased with increasing domain period for $N_x \leq 6$, while it increased for $N_x \geq 6$. The stable domain period in the film was determined by an energetic competition between the advantage of the screening of depolarizing field by breaking the system into domains and the cost of the domain wall formation energy: a longer domain period lowers the energy cost to form domain walls, but leads to insufficient screening of the depolarizing field, and vice versa. The Ti-centered domain configuration with a period of $N_x = 6$ was the most favorable for a film with $m = 3$, due to its minimum energy. In addition, the negative energy difference indicates that the system prefers the ferroelectric polydomain

state to the paraelectric state. This result agrees with experimentally observed 180° stripe domain patterns of $N_x = 6$ in a PbTiO_3 thin film of the same thickness ($m = 3$) grown on SrTiO_3 [4], which supports the reliability of our DFT calculations. For thinner films of $m = 2$ and 1, the Pb-centered domain with a period of $N_x = 4$ and the Ti-centered domain with an $N_x = 2$ configuration, respectively, are energetically favored over the paraelectric state. It should be noted that the ferroelectric single-domain free-standing film was energetically unstable because of the existence of nontrivial depolarizing field, which brings the system back to a paraelectric configuration. This suggests that the depolarizing field [14] in the films can be sufficiently cancelled out only by the formation of domains, even in the thinnest, one unit-cell thick ($m = 1$) film, without any screening effect of electrodes. Therefore, no intrinsic critical thickness for ferroelectricity exists in free-standing ultrathin films.

We briefly mention that as the film thickness decreased ($m = 3, 2$, and 1, respectively), the stable domain period became shorter ($N_x = 6, 4$, and 2, respectively). This trend corresponds well with the experimentally observed relationship between film thickness and domain period in thicker

film [16].

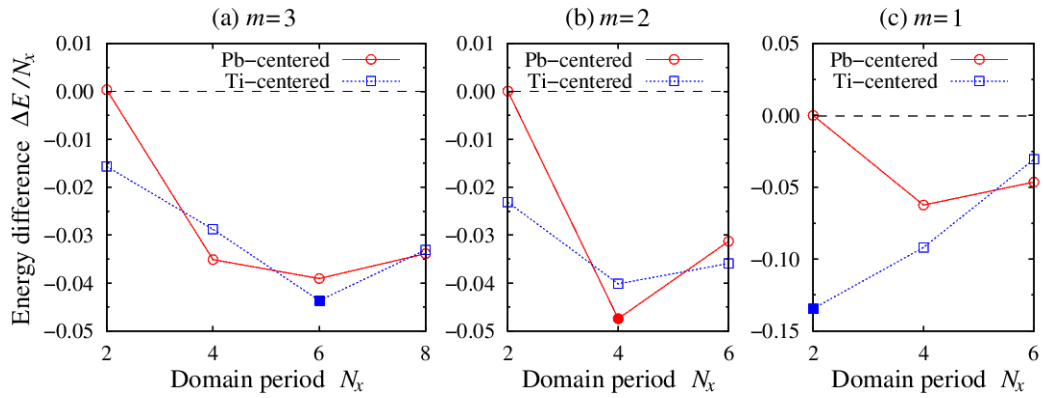


Fig.2.2 Total energy difference between the ferroelectric polydomain and paraelectric phases as a function of the domain period, N_x , for the (a) $m=3$, (b) $m=2$, and (c) $m=1$ unit-cell thick films with the TiO_2 -terminated (001) surfaces. Full symbols indicate the minimum for each film thickness.

2.3.2 Polarization pattern in polydomain PbTiO₃ films

Ferroelectricity in polydomain PbTiO₃ films is investigated by introducing a site-by-site local polarization, P , which can be evaluated by

$$P = \frac{e}{\Omega_c} \sum_j w_j Z_j^* u_j \quad (1)$$

where Ω_c , e and u_j denote the volume of the unit cell, the electron charge, and the atomic displacement vector from the ideal lattice site of atom j , respectively. Index j runs over all atoms in the unit cell i . Z_j^* is the Born effective charge tensor of the cubic bulk PbTiO₃. In this study, we used the theoretical values of the Born effective charge tensors calculated by Zhong *et al.* [16] The local polarization is calculated for each Ti-edged unit cell in the film shown as dashed lines in Fig.2.1. Weights are set to $w_{\text{Pb}} = 1$, $w_{\text{Ti}} = 1/8$ and $w_{\text{O}} = 1/2$, which correspond to the number of unit cells that share the atom.

Figure 2.3 shows the local polarization distribution in a three unit-cell thick film ($m = 3$) of a stable Ti-centered domain having a period of $N_x = 6$. Remarkably, an in-plane polarization (in the x direction) was found near the junction between the surface and domain wall set initially [see red-colored values in Fig.2.3(a)]. As a consequence, a closure domain structure,

where polarization direction was aligned to form a closed flux, was formed in the film [see Fig.2.3(b)]. Note that such closure domains were also formed in the thinner films of $m = 2$ and 1, as well. The closure domains were first proposed in ferromagnetic systems by Landau and Lifshitz [17], and Kittel [4]. Moreover, in recent years, Aguado-Puente and Junquera [18] have theoretically proven the existence of closure domains in ultrathin $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ ferroelectric capacitors. In our model, the closure domain structure seems to consist of not only the 180° domain wall but also the 90° domain wall as Kittel proposed, which can clearly be seen in the vector field of the polarization distribution [see also Fig.2.3(c) for a schematic illustration]. This will be discussed later, in terms of the covalent Pb-O bonding structure in the film. The formation of closure domains can considerably reduce the depolarizing field with respect to only the 180° domain wall configuration, because the in-plane polarization at the surface does not produce any surface charges [19]. Thus, more effective screening of the depolarizing field was realized by the formation of closure domains, which stabilized ferroelectric distortions in the ultrathin films.

On the other hand, the spontaneous polarization was along the normal z

direction to the surface at the center of the domains, where there were two distinct cases of spontaneous polarization directed toward the (i) outside of the film, $P_{\uparrow}$, and (ii) inside of the film, $P_{\downarrow}$ [see also Fig.2.3(b) for the location]. The magnitude of polarizations $P_{\uparrow}$ and $P_{\downarrow}$, was reduced by about 55% and 25%, respectively, with respect to that of the bulk. This indicated that the presence of the surface suppressed the ferroelectricity.

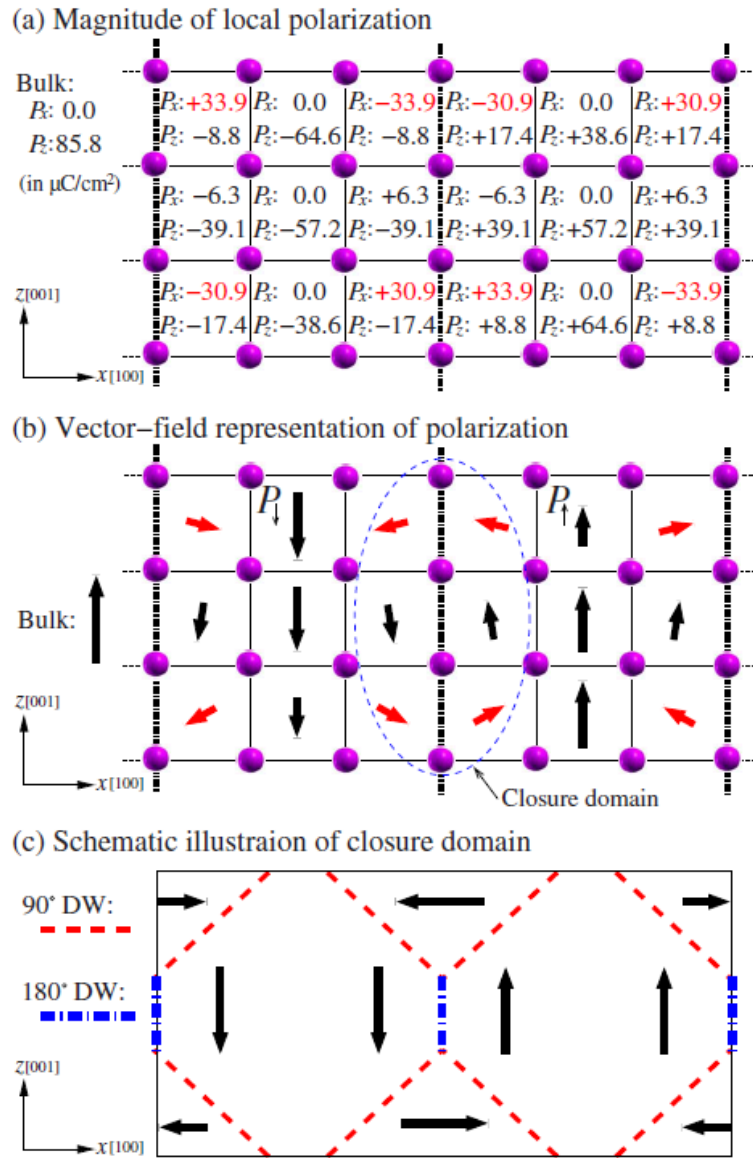


Fig.2.3 Local polarization distribution in a three unit-cell thick film ($m = 3$) of a stable Ti-centered domain having a period of $N_x = 6$: (a) magnitude of local polarization in the x and z directions, P_x and P_z . (b) Vector-field representation of local polarization. The purple spheres indicate Ti atoms. The vertical dotted-dashed lines indicate the initial position of 180° DWs. (c) Schematic illustration of the closure domain structure in the film consisting of the 90° and 180° domain walls. Arrows indicate the polarization direction in each domain.

2.3.3 Atomic and electronic structure of closure domains in PbTiO_3 films

Figure 2.4 shows the atomic displacement from the paraelectric state in a three unit-cell thick film ($m = 3$) of a stable Ti-centered domain having a period of $N_x = 6$. The displacement of atoms forms a closure-type flux across the domain wall. This displacement pattern corresponds well to the polarization orientation of closure domains described in the previous section. A similar closed-flux displacement pattern was observed in the thinner films with $m = 2$ and 1. Remarkably, in-plane (the x direction) atomic displacement was found in the first and second surface layers of the film, which aligned the polarization parallel to the surface. In other words, the in-plane displacement played a significant role in the formation of closure domains, which stabilized the ferroelectric state in the film. In fact, the system turns back to the paraelectric state when the in-plane relaxation was neglected by constraining the x component of atomic coordinates. The displacement of closed flux was also observed in $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ capacitors [18], when a closure domain was formed. It should be noted that only the displacement of Ti atoms was dominant in the

SrRuO₃/BaTiO₃/SrRuO₃ capacitors, while the displacement of Pb atoms is much more active in the ultrathin PbTiO₃ film. This difference originates from the bonding nature of PbTiO₃ and BaTiO₃: the strong covalent Pb-O bond through the hybridization of the Pb 6s and O 2p orbitals plays a critical role in stabilizing large ferroelectric distortions in PbTiO₃ [20], while in BaTiO₃ only the Ti-O bond is responsible for ferroelectricity because of the ionic Ba-O interaction [21]. In fact, displacement of the Ba atom was inactive in SrRuO₃/BaTiO₃/SrRuO₃ capacitors. Thus, the covalent Pb-O bond often characterizes ferroelectricity in PbTiO₃ nanofilms.

Figure 2.5 shows the atomic configuration and charge density distribution on the PbO (010) plane in a film three unit-cell thick ($m = 3$). Those of the isolated 180° and 90° domain walls are also shown for comparison. Here, the covalent Pb-O bonds of interest are emphasized by white lines. For the single-domain bulk with the polar axis of [001], the Pb-O bond formed a zigzag shape along the [100] direction. In the film, on the other hand, this zigzag bonding structure was terminated and switched to the inverse structure across the center of area A (see the white solid

lines). This bonding sequence was characteristically similar to that of the 180° domain wall, where the polarization direction changes from upward on one side to downward on the other. Meanwhile, a “ $\sqsupset$ ”-type series of Pb-O bonds was found in the area B of the film, which corresponds well to the bonding sequence in the 90° domain wall (see the white solid lines) [22]. This indicates that the 180° and 90° domain walls were formed in the center of area A and in area B, respectively. Therefore, the closure domain structure in the PbTiO_3 film consists of both the 180° and 90° domain walls, as illustrated in Fig.2.3(c).

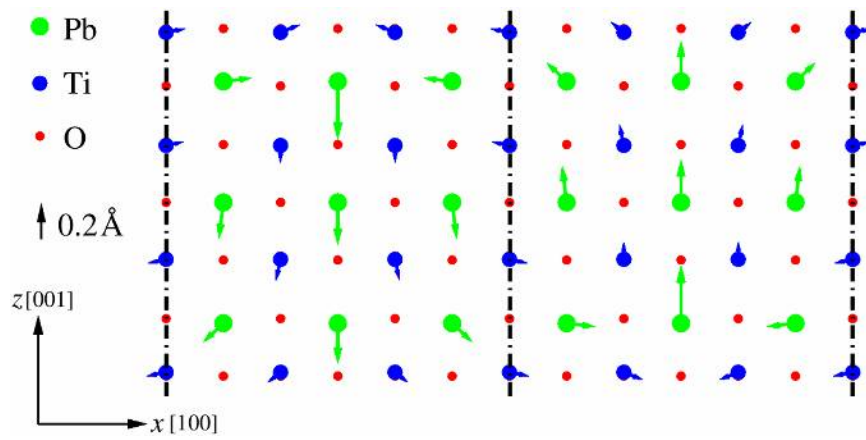


Fig.2.4 Atomic displacement from the paraelectric state in a three unit-cell thick film ($m = 3$) of a Ti-centered domain having a stable period of $N_x = 6$. Only the displacement of cations (Pb and Ti) is depicted for clarity. The vertical dotted-dashed lines indicate the initial position of 180° domain walls.

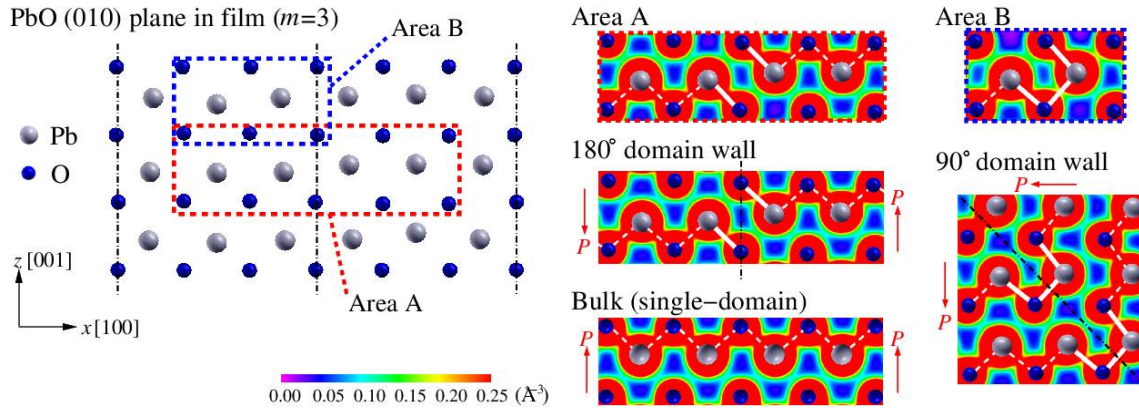


Fig.2.5 Atomic configuration and charge density distribution of the PbO (010) plane in a PbTiO₃ film three unit-cell thick ($m = 3$) of a Ti-centered domain having a stable period of $N_x = 6$. Those of the isolated 180° and 90° domain walls and the bulk are shown for comparison. Covalent Pb-O bonds are emphasized by white lines and solid and dashed lines indicate the Pb-O bonds observed near the domain walls and in the bulk, respectively. The dotted-dashed lines indicate the domain walls. Arrows, P , denote the polarization direction in each domain.

2.4 Conclusions

Ab initio (first-principles) DFT calculations were performed to elucidate the detailed polarization pattern and the atomic structure in the ultrathin films with below 1.2nm thickness was investigated.

In a three unit-cell thick film ($m=3$), the ferroelectric polydomain state with the six unit-cell domain period ($N_x=6$) was found to be energetically favorable over the paraelectric state, which is consistent with experimentally observed 180° stripe domain patterns. Further studies of the thinner films ($m=2$ and 1 unit-cell thick) revealed that the ferroelectric polydomain phase was also stabilized by the formation of domains with shorter periods of $N_x=4$ and 2, respectively. This suggests that no critical thickness for ferroelectricity exists in free-standing polydomain films.

Local polarization analysis determined that the polarization direction aligned as a closed flux in the film. This indicates that a closure domain structure as first proposed by Kittel was formed. Remarkably, in-plane atomic displacement was found in the surface layer, which leads to an in-plane polarization component. Since the in-plane polarization does not induce surface charges, which would create a depolarizing field, the

formation of a closure domain plays a central role in stabilizing the ferroelectric polydomain state in ultrathin films.

The charge density distributions indicated that the closed-flux displacement of Pb atoms leads to reconstruction of the covalent Pb-O bonds in the film. The resulting bonding structures at the center of the film and at the surface were found to be characteristically similar to the 180° and 90° domain walls, respectively. This indicates that the closure domain structure consists of both the 180° and 90° domain walls.

References

- [1] Ramesh, R., Thin Film Ferroelectric Materials and Devices, (1992).
- [2] Batra, I.P. and Silverman, B.B, Solid State Commun, **11**, 291, (1972)
- [3] Mehta, R.R., Silverman, B.D, and Jacobs, J.T., Journal of Applied Physics, **44**, 3379, (1973).
- [4] C. Kittel, *Physical Review*, **70**, 965 (1946).
- [5] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, C. Thompson, Science, 304, 1650 (2004).
- [6] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Physical Review*, **136**, B864 (1964).
- [7] W. Kohn and L. Sham, Self-consistent equations including exchange and correlation effects, *Physical Review*, **140**, A1133 (1965).
- [8] G. Kresse and J. Hafner, Physical Review B, **47**, 558 (1993).
- [9] G. Kresse and J. Furthmüller, Physical Review B, **54**, 11169 (1996).
- [10] P. E. Blöchl, Physical Review B, **50**, 17953 (1994).
- [11] G. Kresse and D. Joubert, Physical Review B, **59**, 1758 (1999).
- [12] D.M. Ceperley and B. J. Alder, Physical Review Letter, **45**, 566 (1980).

- [13] R. I. Egilits and D. Vanderbilt, Physical Review B, **76**, 155439 (2007).
- [14] N. Sai, A. M. Kolpak, and A. M. Rappe, Physical Review B, **72**, 020101 (2005).
- [15] S. K. Streiffer, J. A. Eastman, D. D. Fong, C. Thompson, A. Munkholm, M. V. Ramana Murty, O. Auciello, G. R. Bai, and G. B. Stephenson, Physical Review Letter, **89**, 067601 (2002).
- [16] W. Zhong, R. D. King-Smith, and D. Vanderbilt, Physical Review Letter, **72**, 3618 (1994).
- [17] L. Landau and E. Lifshitz, Physical Z Sowjentunion, **8**, 153 (1935).
- [18] P. Aguado-Puente and J. Junquera, Physical Review Letter, **100**, 177601 (2008).
- [19] T. Shimada, K. Wakahara, Y. Umeno, and T. Kitamura, Journal of Physics Condensed Matter ,**20** ,325225 (2008).
- [20] R. E. Cohen, Nature (London), **358**, 136 (1992).
- [21] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata, and M. Sakata, Physical Review Letter, **87**, 217601 (2001).
- [22] T. Shmiada, Y. Umeno, and T. Kitamura, Physical Review B, **77**, 094105 (2008).

Chapter 3 Ferroelectricity and strain effect at surface steps in PbTiO_3 nanofilms

3.1 Introduction

Several experimental study and density functional calculations [1,2] have investigated the surface structures of PbTiO_3 and BaTiO_3 [3-9]. In fact, on the (001) surface of the perovskite type oxides, surface step is often observed [10,11]. The surface step characteristically possesses an atomically sharp edge structure consisting of (100) and (001) surfaces [12-15]. The coordination number at surface step changes more drastically than flat (001) surface, and the atomic and electronic structure are disarranged dynamically. So that, it is necessary to reveal the effect of surface step for the polarization pattern. Against the surface step consisting of (100) and (001) flat surface in the nanofilm, there are three typical polarization directions, [100], [010] and [001] directions. First of all, we investigate the surface step with polarization along [010] direction, because this situation is the most simple for understanding the effect of coordination number due to no surface polarization charge.

In this chapter, we perform *ab initio* density functional theory calculations to investigate ferroelectricity at PbTiO_3 surface steps with atomically sharp edges consisting of (100) and (001) surfaces. The crucial role of in-plane strain for the polarization pattern is also investigated.

3.2 Simulation procedure

Ab initio calculations based on the density-functional theory are conducted using the Vienna *Ab initio* Simulation Package (VASP) [16,17]. The electronic wave functions are expanded in-plane waves up to a cutoff energy of 500 eV. The pseudopotentials based on the projector augmented wave (PAW) method [18,19] explicitly include the O $2s$ and $2p$, the Ti $3s$, $3p$, $3d$ and $4s$, and the Pb $5d$, $6s$ and $6p$ electrons in the valence states. The local-density approximation (LDA) of the Ceperley-Alder form [20, 21] is employed to evaluate the exchange-correlation energy.

Figure 3.1 shows the simulation model of a nine-layer PbTiO_3 film with surface steps. The surface step consists of (100) and (001) surfaces with a one-unit-cell step height and a four-unit-cell terrace width. The surface terminations of both the PbO and TiO_2 atomic layers are considered (see figures 3.1(a) and (b), respectively), because ferroelectricity is highly

dependent on the termination layer at the (001) surface [3-5]. Spontaneous polarization is initially aligned along the [010] step edge (in the y direction). Since a three-dimensional periodic boundary condition is applied, a vacuum region of $l_v = 12 \text{ \AA}$ is introduced in the z direction to avoid undesirable interactions from adjacent films. The simulation cell vectors are therefore set to $\mathbf{a}_1 = (4a, 0, -a)$, $\mathbf{a}_2 = (0, c, 0)$ and $\mathbf{a}_3 = (0, 0, 4a+l_v)$, where a and c are the theoretical lattice constants of the bulk: $a = 3.867 \text{ \AA}$ and $c = 4.034 \text{ \AA}$ ($c/a = 1.043$). Brillouin zone (BZ) integrations are carried out using a $2 \times 6 \times 2$ Monkhorst-Pack k-point [22] mesh with a Gaussian smearing of 0.20 eV. For descriptive purposes, the unit cells around the surface step structure are referred to as ‘step site’, ‘upper terrace’, ‘lower terrace’ and ‘inside’, as depicted in figure 3.1.

To obtain the fully-relaxed equilibrated surface step structure, the atomic positions and the cell dimensions in the x and y directions are relaxed using the conjugate-gradient (CG) method until all Hellmann-Feynman forces and the stress components of σ_{xx} and σ_{yy} $2.5 \times 10^{-3} \text{ eV \AA}^{-1}$ and 0.05 GPa, respectively.

Here, we additionally investigate the role of uniaxial strain, which

changes both the magnitude and direction of polarization in ferroelectric materials. Also, the application of uniaxial strain to freestanding thin films can be experimentally done by tensile loading tests [23]. To investigate the effect of strain on the ferroelectricity at the surface step, a small incremental strain in the y direction, $\Delta\epsilon_{yy}$, is applied to the simulation model in a stepwise manner. At each strain, the atomic coordinates are relaxed using the structural optimization described above.

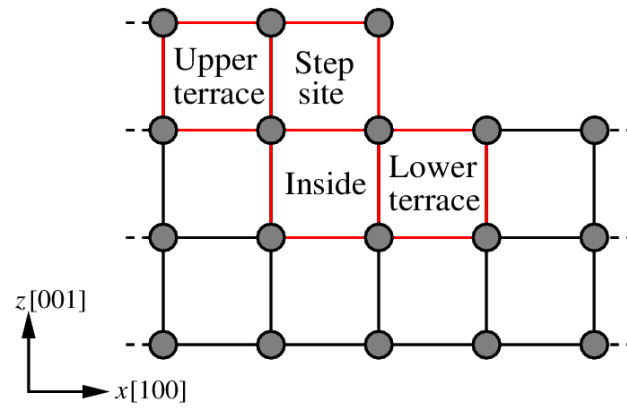
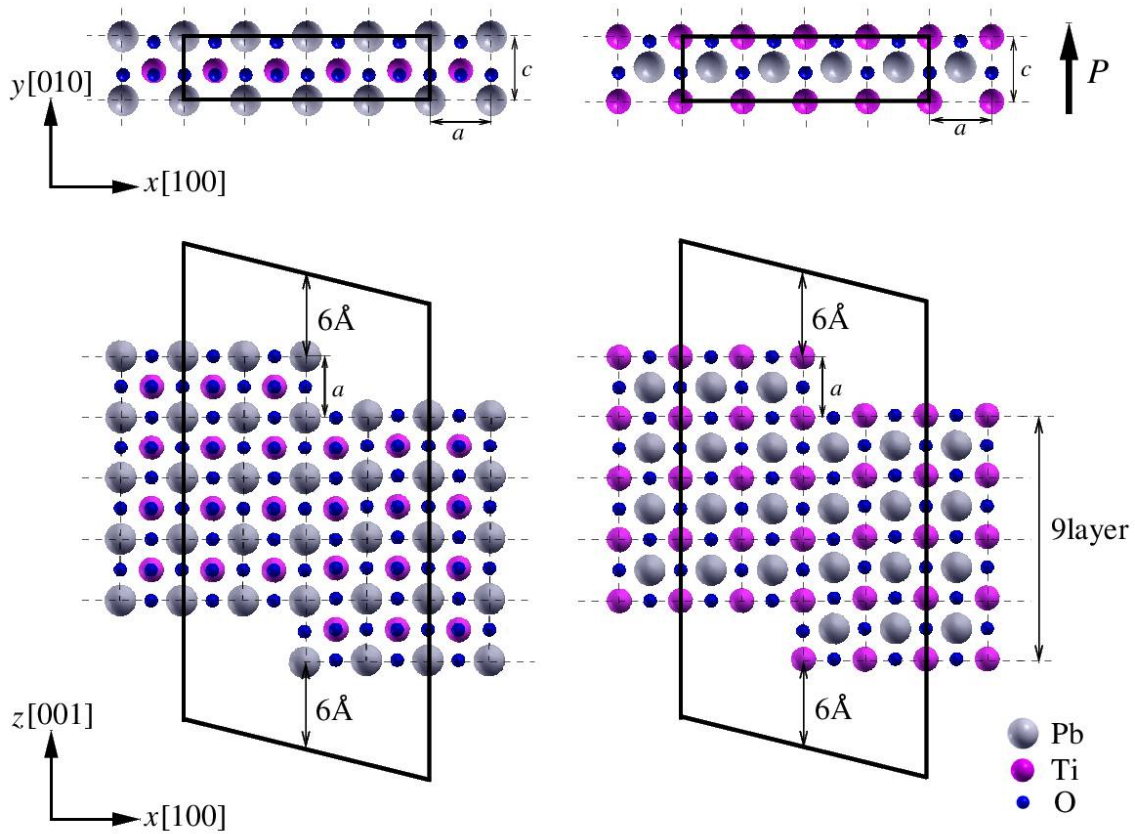


Fig.3.1 Simulation models of nine-layer PbTiO₃ films with (a) PbO-terminated and (b) TiO₂-terminated surface steps consisting of (100) and (001) surfaces. Spontaneous polarization, $\mathbf{P}$, aligns in the [010] (y) direction. The solid boxes represent the simulation supercells. (c) Schematic illustration of site names in the surface step structure.

3.3 Results and discussion

3.3.1 Polarization pattern at unstrained surface steps

Ferroelectricity at the surface step is investigated by introducing a site-by-site local polarization, P , which can be evaluated by equation (1) as shown in Chapter 2. The local polarization is calculated in each Pb-edged and Ti-edged unit cell of PbO-terminated and TiO₂-terminated surface steps as shown by the dashed lines in fig.3.1 (a) and (b), respectively. Weights are set to $w_{\text{Pb}} = 1/8$, $w_{\text{Ti}} = 1$ and $w_{\text{O}} = 1/2$ for the Pb-edged cell, and $w_{\text{Pb}} = 1$, $w_{\text{Ti}} = 1/8$ and $w_{\text{O}} = 1/4$ for the Ti-edged cell. These correspond to the number of unit cells that share the atom.

Figure3.2 shows the local polarization distribution calculated using equation (1) for PbO-terminated and TiO₂-terminated surface steps. For comparison, the results for the bulk and for a [010]-polarized nine-layered film with flat (001) surfaces are also shown, as ‘bulk’ and ‘surface’, respectively. For ‘surface’, we take the value of the unit cell at the surface of a [010]-polarized nine-layered film. For the PbO-terminated surface step, the step site exhibits the highest polarization in the y direction of $P_y = 108.2 \mu\text{Ccm}^{-2}$, this is approximately 20% greater than that of the bulk (85.8

μCcm^{-2}). The local polarizations in the upper and lower terraces, which are the second and third highest polarizations, respectively, are nearly equal to that of the (001) surface. The inner cells of the slab have a polarization comparable to that of the bulk, which implies that the effect of the surface step extends to a depth of nearly one unit cell below the surface layer. In contrast, the local polarization P_y is lower than the bulk value at TiO_2 -terminations, especially at the step site, where it is 19% lower than the bulk value. In summary, ferroelectricity is locally enhanced at PbO -terminated surface steps, and suppressed at TiO_2 -terminations. In addition, a z -component is found in step sites ($P_z = -21.9$ and $-37.1 \mu\text{Ccm}^{-2}$ for the PbO - and TiO_2 -terminations, respectively), whereas the other sites exhibit very low P_z values. This indicated that spontaneous polarization is locally rotated toward the inside of the film at step edges.

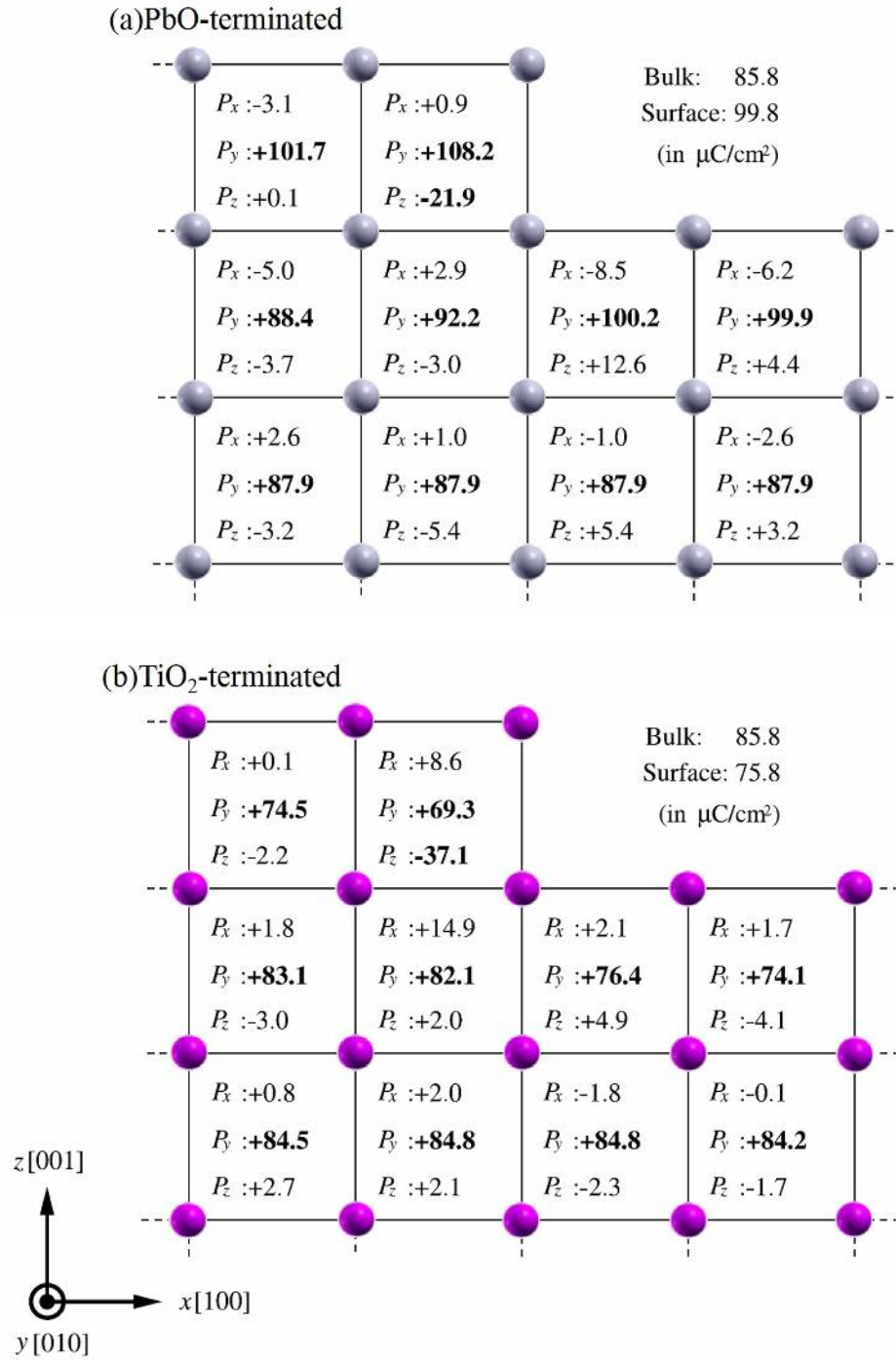


Fig3.2 Local polarization distribution calculated using equation (1) of (a) PbO-terminated and (b) TiO₂-terminated surface steps (in μCcm^{-2}). Only the upper side of the simulation models is shown due to symmetry. Gray and purple spheres indicate Pb and Ti atoms, respectively.

3.3.2 Atomic and electronic structure of unstrained surface steps

It has already been demonstrated that the strong ferroelectric distortions and high lattice tetragonality in PbTiO_3 originate from the formation of covalent Pb-O bonds through the hybridization of the Pb 6s and O 2p orbitals [24,25], whereas the Ba-O interaction is almost ionic in BaTiO_3 , which has a considerably weaker polarization than PbTiO_3 . Therefore, we discuss the electronic structure of the surface step by focusing on the covalent Pb-O bond. Figure 3.3 shows the difference in the site-by-site minimum charge density along Pb-O and Ti-O bonds from the corresponding site of the bulk, $\Delta\rho_{\min}$, for PbO-terminated and TiO_2 -terminated surface steps. In the PbO-terminated surface step, the charge density of the Pb-O bond increases remarkably at the edge in the step site. This is because the Pb atom at the edge has a smaller coordination number than in the bulk, so that more electrons contribute to the bond. Thus, the electron concentration in the edge bond due to the reduced coordination number results in locally enhanced ferroelectricity at the step site. On the other hand, the charge density increases at the Ti-O bond,

especially at the edge of the TiO_2 -terminated surface steps, whereas it decreases slightly at the Pb-O bond. This indicated that the electrons transfer from Pb-O sites to Ti-O sites. The strengthening of the Ti-O bond at the step site can be explained in the same manner as that of the Pb-O bond at the PbO-terminated surface step. As a result of charge redistribution, the covalent Pb-O bond is weakened, suppressing ferroelectricity at the TiO_2 -terminated surface step. Thus, ferroelectricity at the PbTiO_3 surface step depends significantly on the termination.

(a) PbO-terminated

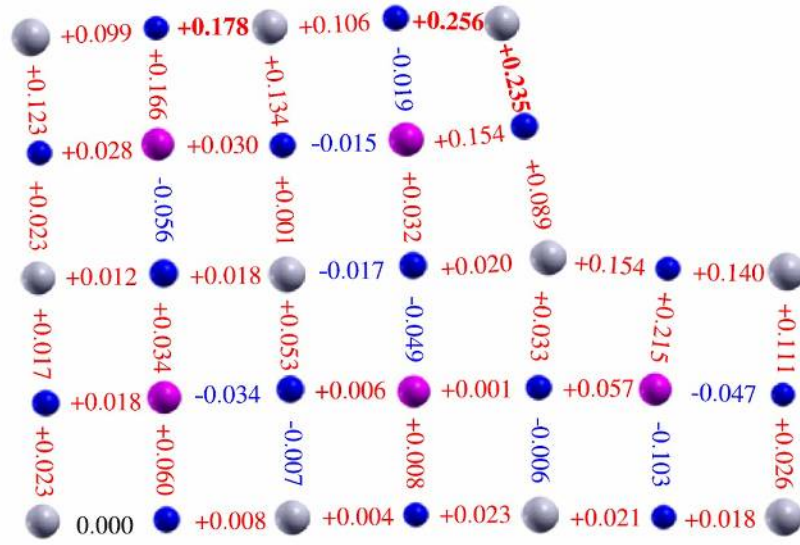
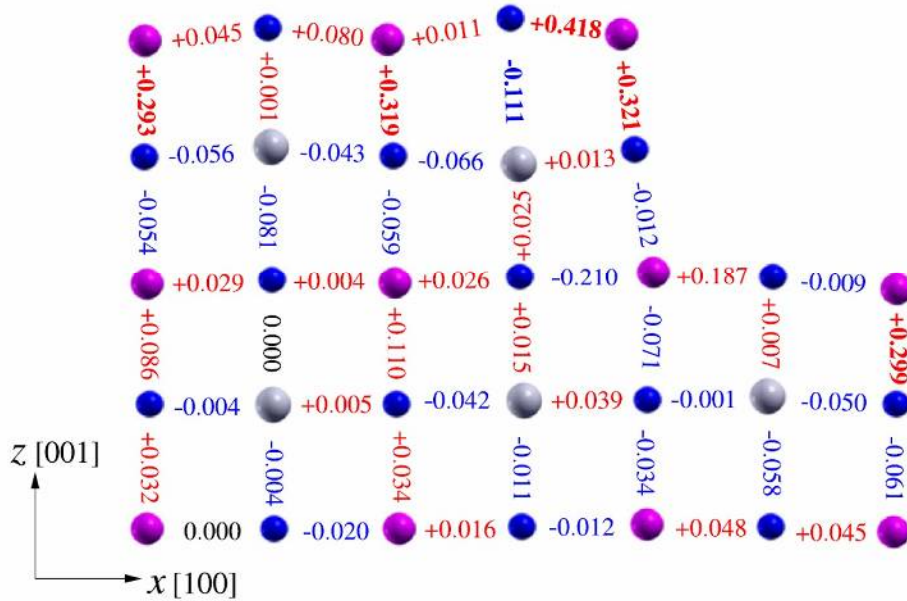
(b) TiO₂-terminated

Fig.3.3 Difference in site-by-site minimum charge density along Pb-O and Ti-O bonds from the corresponding site in the bulk, $\Delta\rho_{\min}$ (in $\text{\AA}^{-3}$), for (a) PbO-terminated and (b) TiO₂-terminated surface steps. The numbers in red and blue indicate the increase and decrease, respectively. Gray (light gray), purple (dark gray), and blue (blank) spheres indicate Pb, Ti, and O atoms, respectively.

3.3.3 Influence of tensile and compressive strains for polarization pattern

Figure 3.4 shows the x , y , and z components of the site-by-site local polarization as a function of strain ε_{yy} for the PbO-terminated surface step. The local polarization P_y increases nearly linearly with respect to the applied tensile strain at all sites. This indicates that the tensile strain tends to enhance the ferroelectricity, because it increases the tetragonality of the PbTiO₃ lattice, which is strongly coupled to the ferroelectric distortions. On the other hand, P_y decreases as the compressive strain is applied (see the negative value of strain ε_{yy}). Note that the same trend is also observed for TiO₂-terminations. At a strain of $\varepsilon_{yy} = -0.05$, the magnitudes of P_x and P_z begin to increase at all sites, whereas they remain almost unchanged under tension. This suggests that the polarization direction rotates from the y direction to the x - z plane at the critical strain. Remarkably, the change in P_x and P_z differs by site, indicating that the spontaneous polarization is not uniform in the x - z plane near surface steps.

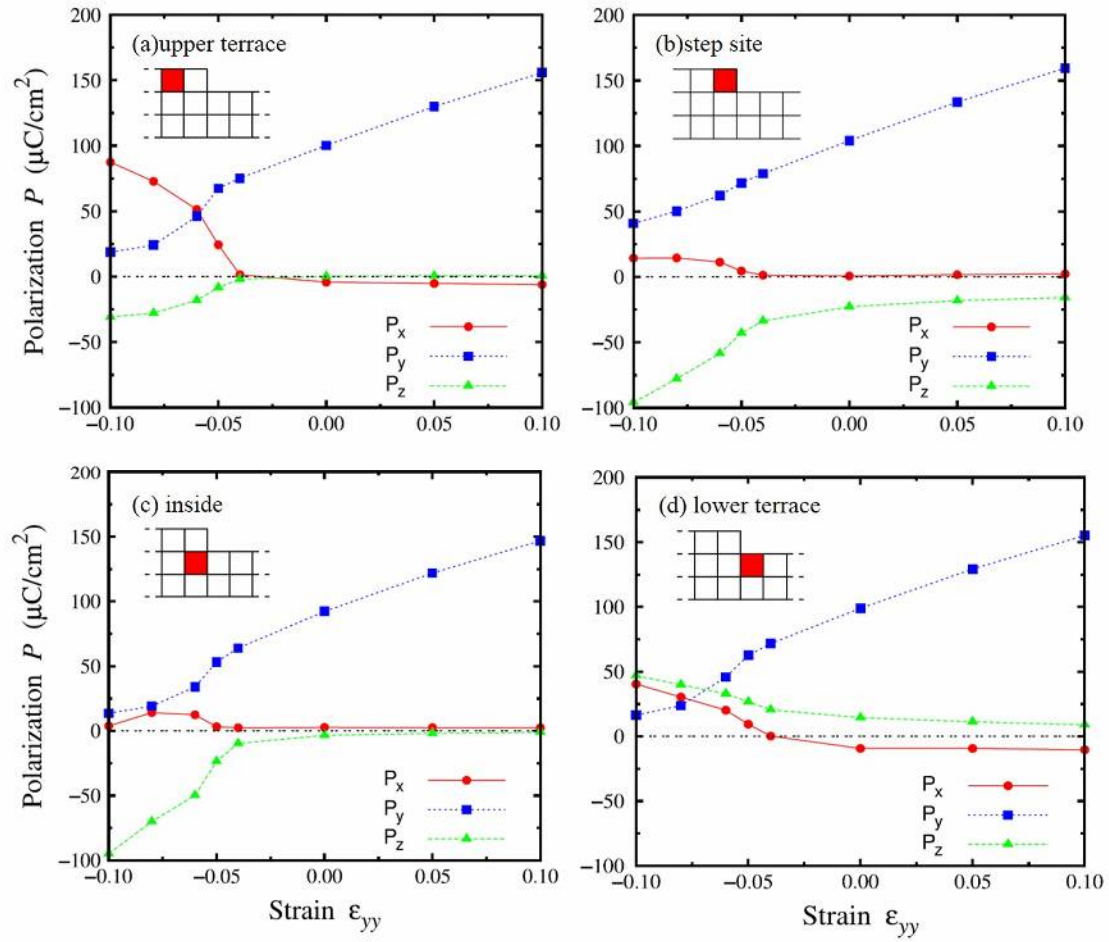


Fig.3.4 Site-by-site local polarization as a function of strain ϵ_{yy} for the PbO-terminated surface step: (a) upper terrace, (b) step site, (c) inside, and (d) lower terrace.

Figure 3.5 depicts the vector field of the local polarization distribution of the PbO-terminated surface step at a strain of $\varepsilon_{yy} = -0.05$. The polarization is aligned in the $-z$ direction on the left side of the surface step, which is in the step site before the critical strain, whereas the opposite rotation occurs (in the $+z$ direction) on the right side. This indicates that the surface step divides into domains on the formation of a 180° domain wall along the surface step edge, as indicated by the dotted-dashed line in figure 3.6(a). This result is consistent with the experimental observation that 180° stripe domains form along the surface step edges in PbTiO_3 thin films epitaxially grown on $\text{SrTiO}_3(001)$ substrates [26]. This comparison is reasonable because PbTiO_3 thin films should have the same geometry as the substrate and the lateral lattice parameters of our model under the strain, $3.86 \text{ \AA}$ and $3.84 \text{ \AA}$ in the x and y directions, respectively, are almost the same as the lattice parameter of the substrate SrTiO_3 of $a = 3.85 \text{ \AA}$. Remarkably, the local polarization tends to lie along the surface (the x direction) in both the upper and lower terraces, whereas the polarization is aligned in the z direction within the film. As a result, the polarization forms a flux along the surface step and the domain wall. In terms of the

polarization distribution pattern, the domain configuration at the surface step seems to consist of not only the 180° , but also 90° domain walls, as schematically illustrated in figure 3.5(b). This is confirmed from the covalent Pb-O bonding structure, as will be discussed later. Note that since the same domain configuration is formed for the TiO_2 -terminated surface steps under compression, this ferroelectric polydomain state is not a special case for PbO-terminations.

The formation of a polydomain structure at the surface step can be reasonably explained in terms of the depolarizing fields as follows. For ferroelectric thin film with a polar axis perpendicular to its surface, the termination of polarization at surface produces surface charges. These surface charges create a depolarizing field that destabilizes ferroelectric distortions [27, 28]. On the other hand, polarization parallel to the surface does not produce any surface charges so that no depolarizing field is generated. A ferroelectric system generally breaks up into domains to minimize the electrostatic energy of the depolarizing fields. By the formation of domains at the surface step, as shown in figure 3.5(b), the surface charge that generates a depolarizing field may be sufficiently

compensated because all the polarizations are parallel to the surface step. Hence, the polydomain structure shown can reasonably stabilize the ferroelectric distortions at the surface step because the polydomain configuration does not generate any depolarizing field that destabilizes the ferroelectric distortions. This result suggests that a polydomain structure is one possibility for the ferroelectric structure at the surface step. Based on this polydomain structure, if a 180° domain wall was not located along the surface step edge, a polarization perpendicular to the surface would appear and the resulting depolarizing field would destabilize the ferroelectric distortions at the surface step. This suggests that the 180° domain wall prefers to exist at the surface step edge. A similar but different domain configuration with a closed-flux polarization has been reported to form in ferroelectric ultrathin films with flat (001) surfaces and ultrathin capacitors of $\text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3$ (SRO/BTO/SRO). The formation of a closed-flux domain, which is known as a ‘closure domain’ first proposed by Landau and Lifshitz [29] and Kittel [30] for a ferromagnetic system, could also compensate the depolarizing fields by aligning the polarizations along the surface, thereby stabilizing the ferroelectric state. Consequently,

ferroelectric nanofilms should be characterized by a polydomain configuration similar to that found at the surface step in the present study.

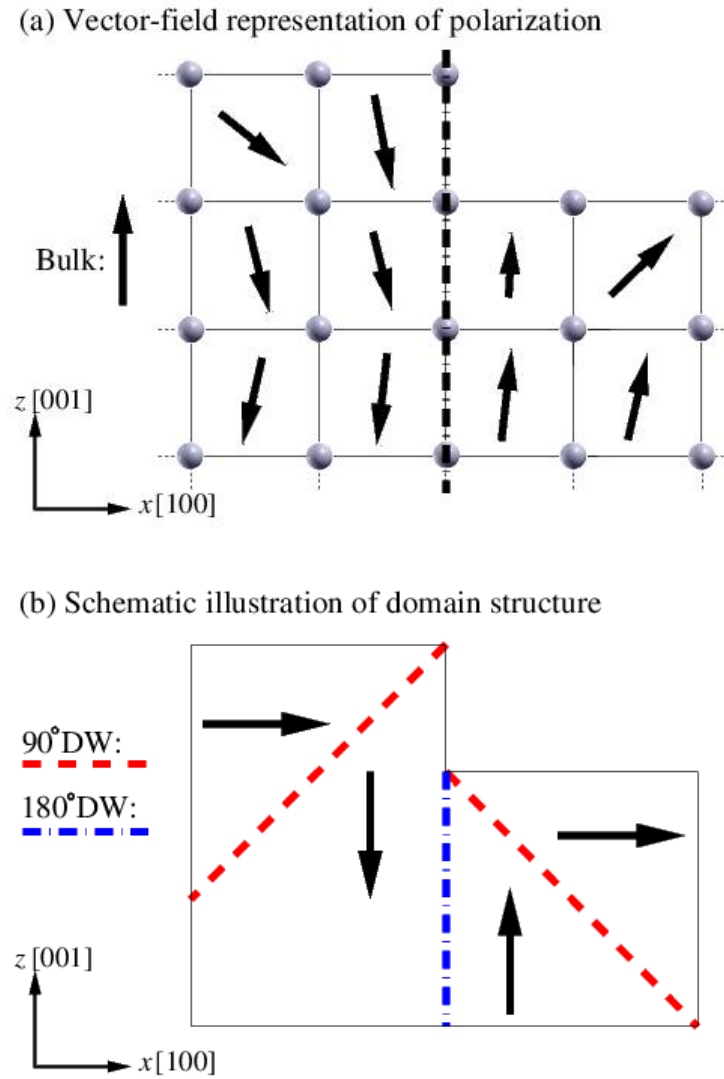


Fig.3.5 (a) Vector-field representation of local polarization distribution of the PbO-terminated surface step at a strain of $\epsilon_{yy} = -0.05$. (b) Schematic illustration of the domain configuration at the PbO-terminated surface step. The dashed and dashed-dotted lines indicate the 180° and 90° domain walls, respectively. Arrows indicate the polarization direction in each domain.

Figure 3.6 shows the atomic configuration and charge density distribution on the PbO (010) plane of the PbO-terminated surface step at a strain of $\varepsilon_{yy} = -0.05$. Those of the isolated 180° and 90° domain walls and the bulk are shown for comparison. The covalent Pb-O bonds of interest are emphasized by white lines. For the bulk with a polar axis of [001], the Pb-O bond forms a zig-zag type bonding structure along the [100] direction (see the white dashed lines). On the other hand, such a zig-zag bonding is terminated and reverses direction across the center of area A of the surface step (see the white solid lines). This bonding sequence corresponds to that of a 180° domain wall, where the polarization direction changes from upward on one side to downward on the other side. A ‘ $\sqsupset$ ’-shape bonding structure is observed in areas B and C of the surface step, which corresponds well to the characteristic bonding sequence at a 90° domain wall (see the white solid lines). This indicated that the 180° and 90° domain walls are formed in the center of area A, and in areas B and C. The polydomain configuration at the surface step, therefore, consists of both 180° and 90° domain walls, as illustrated in figure 3.5(b).

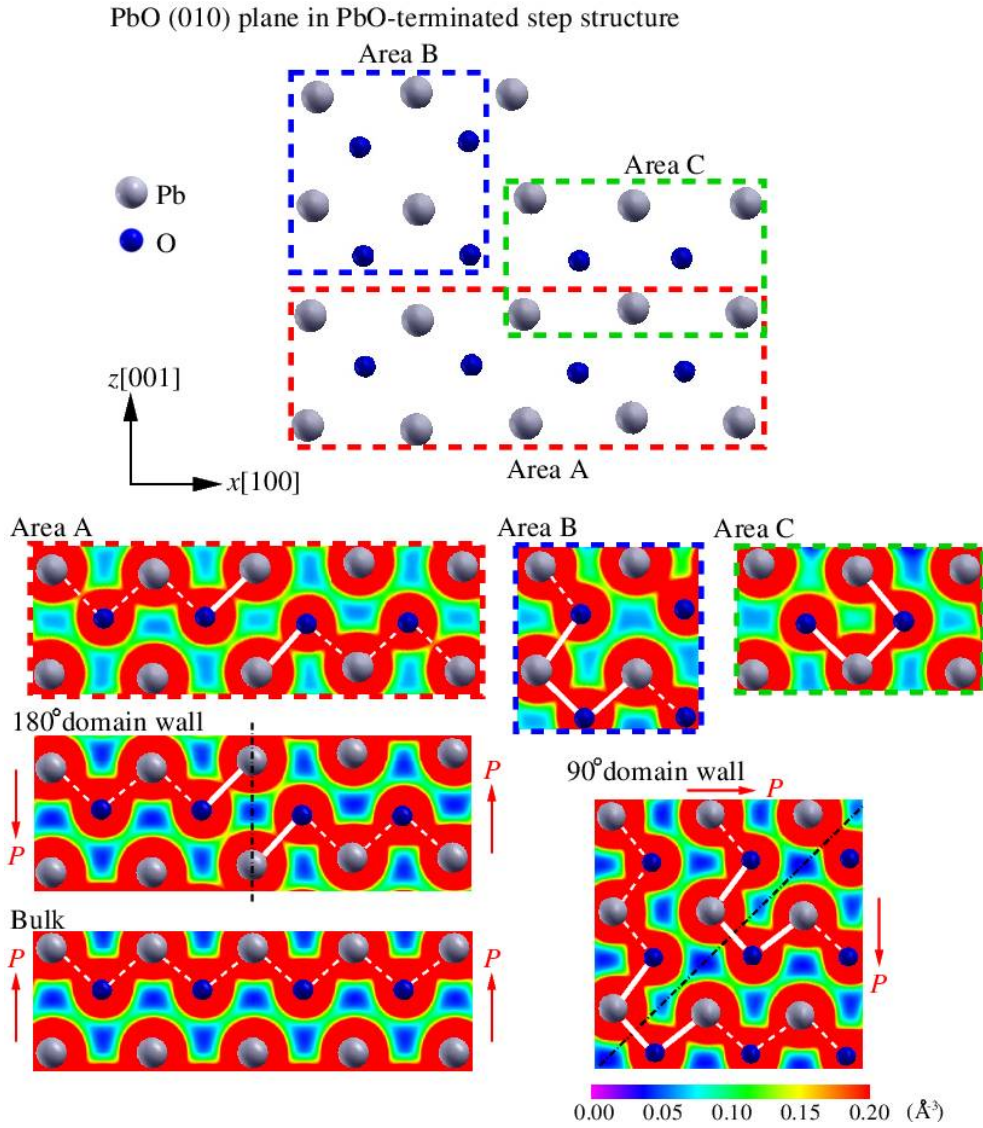


Fig.3.6 Atomic configuration and charge density distribution on the PbO(010) plane of the PbO-terminated surface step at a strain of $\epsilon_{yy} = -0.05$. Those of the isolated 180° and 90° domain walls and the bulk are shown for comparison. Covalent Pb-O bonds are emphasized by white lines, and solid and dashed lines indicate Pb-O bonds observed near the domain walls and in the bulk, respectively. Arrows, P , denote the polarization direction in each domain.

3.4 Conclusions

We investigated ferroelectricity at PbTiO_3 surface steps consisting of (001) and (100) surfaces with a spontaneous polarization along [010] direction. Polarization is locally enhanced at the PbO -terminated surface steps, and suppressed at the TiO_2 -terminated surface steps. The enhancement of ferroelectricity in the PbO -termination is caused by the formation of strong covalent Pb-O bonds at the edge of the surface step. This arises due to an increase in the number of electrons that contribute to the bond because of the low coordination number of the Pb atom at the step edge. On the other hand, the covalent Pb-O bonds are weakened by charge transfer from the Pb-O site to the Ti-O site at the edge of the TiO_2 -terminated surface step, suppressing the ferroelectricity at the surface step.

A tensile strain applied along the [010], ε_{yy} , tends to enhance the ferroelectricity at the surface step, whereas the ferroelectric polarization decreases under compression regardless of the surface termination. At a critical strain of $\varepsilon_{yy} = -0.05$, spontaneous polarization rotates from the [010] direction to the [001] direction. Simultaneously, the surface step is divided into domains along the step. Analysis of the charge density distributions

indicates that the polydomain structure at the surface step consists of both 180° and 90° domain walls. By forming a polydomain structure at the surface step, surface charges that generate a depolarizing field are sufficiently compensated and the ferroelectric distortions at the surface step are stabilized.

References

- [1] P. Hohenberg and W. Kohn, *Physical Review*, **136** B864 (1964).
- [2] W. Kohn and L. Sham, *Physical Review* **140** A1133 (1965).
- [3] B. Meyer, J. Padilla and D. Vanderbilt, *Faraday Discuss*, **114**, 395 (1999).
- [4] C. Bungaro and K. M. Rabe, *Physical Review B* **71** 035420 (2005).
- [5] Y. Umeno, T. Shimada, T. Kitamura and C. Elsässer, *Physical Review B* **74** 174111 (2006).
- [6] R. I. Eglitis and D. Vanderbilt, *Physical. Review. B* **76** 155439 (2007).
- [7] G. Shirane and R. Pepinsky, *Acta Crystallogr.* **9** 131 (1956).
- [8] A. M. Glazer and S. A. Mabud, *Acta Crystallogr. B* **34** 1065 (1978).
- [9] A. Munkholm, S. K. Streiffer, M. V. R. Murty, J. A. Eastman, C. Thompson, O. Auciello, L. Thompson, J. F. Moore and G. B. Strepenson, *Physical Review Letter* **88** 016101 (2001).
- [10] G. B. Cho, M. Yamamoto and Y. Endo, *Thin Solid Films*, **464** 80 (2004).
- [11] K. Takahashi, M. Suzuki, M. Yoshimoto and H. Funakubo, *Journal of Applied Physics*, **45** L138 (2006).

- [12] Y. Yamashita, K. Mukai, J. Yoshinobu, M. Lippmaa, T. Kinoshita and M. Kawasaki, *Surface Science*, **514** 54 (2002).
- [13] E. A. Kotomin, E. Heifets, S. Dorfman, D. Fuks, A. Gordon and J. Maier, *Surface Science* **566** 231 (2004).
- [14] M. W. Chu, I. Szafraniak, R. Scholz, C. Harnagea, D. Hesse, M. Alexe and U. Gösele, *Nature Materials*, **3** 87 (2004).
- [15] J. H. Jeon and S. K. Choi, *Applied Physics Letters*, **91** 091916 (2007).
- [16] G. Kresse and J. Hafner, *Physical Review B* **47** 558 (1993).
- [17] G. Kresse and J. Furthmüller, *Physical Review B* **54** 11169 (1996).
- [18] P. E. Blöchl, *Physical Review B* **50** 17953 (1994).
- [19] G. Kresse and D. Joubert, *Physical Review B* **59** 1758 (1999).
- [20] D. M. Ceperley and B. J. Alder, *Physical Review Letters*, **45** 566 (1980).
- [21] Z. Wu, R. E. Cohen and D. J. Singh *Physical Review B* **70** 104112 (2004).
- [22] H. J. Monkhorst and J. D. Pack *Physical Review B* **13** 5188 (1976).
- [23] H. Huang and F. Spaepen, *Acta Mater.* **48** 3261 (2000).
- [24] R. E. Cohen, *Nature* **358** 136 (1992).

- [25] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata and M. Sakata, *Physical Review Letters*, **87** 217601 (2001).
- [26] C. Thompson, D. D. Fong, R. V. Wang, F. Jiang, S. K. Streiffer, K. Latifi, J. A. Eastman, P. H. Fuoss and G. B. Stephenson, *Applied Physics Letters* **93** 182901 (2008).
- [27] I. P. Batra and B. D. Silverman, *Solid State Commun.* **11** 291 (1972).
- [28] R. R. Mehta, B. D. Silverman and J. T. Jacobs *Journal of Applied Physics* **44** 3379 (1973).
- [29] L. Landau and E. Lifshitz, *Physical Z Sowjetunion* **8** 153 (1935).
- [30] C. Kittel, *Phys. Rev.* **70** 965 (1946).

Chapter 4 Ferroelectricity of domain walls with O-vacancies in PbTiO₃

4.1 Introduction

Oxygen vacancy is the common internal structure, and it has a lot of attention because of the strong effect for the material properties [1-8]. In particular, ferroelectricity that originates from a delicate balance between long-range Coulomb and short-range covalent interactions [9-12], is strongly affected by vacancies because the presence of a vacancy results in a loss of short-range interaction at a local site due to the breaking of a covalent bond, and the charged state of the vacancy additionally leads to an imbalance of the long-range Coulomb interaction.

As mentioned in Chapter 2, nanofilms with polarization perpendicular to the surface have polydomain structure, so that we need to study the relationship among surface, domain wall and vacancy for understanding the complex situation in ferroelectric nanofilms with oxygen-vacancies. Hence, first of all, we investigated the ferroelectricity in domain walls with oxygen-vacancies to understand the complex situation step-by-step.

For investigating the electronic properties of point defects in insulators

and semiconductors, *ab initio* density functional theory (DFT) calculations have been commonly used so far [13,14]. In these previous studies, the local density approximation (LDA) [15] or the generalized gradient approximation (GGA) [16,17] functionals were often employed to describe the exchange-correlation energy within DFT. However, both the LDA and GGA tend to underestimate the band gaps of insulators and semiconductors [18-29]. The LDA and GGA describe the conduction bands instead of the defect states, which leads to a critical misprediction of the electronic structures of point defects. Hybrid Hartree-Fock (HF) density functional [30] includes in part the exact nonlocal exchange of HF theory to DFT and has been shown to accurately reproduce the band gaps of insulators and semiconductors. Therefore, for an accurate description of the defect physics, the use of the hybrid functional is indispensable.

In this study, we investigate the ferroelectricity of 180° domain walls with oxygen-vacancies in PbTiO_3 using first-principles calculations based on the hybrid HF density-functional calculations.

4.2 Simulation procedure

We conducted ab initio calculations [14] using the Vienna Ab initio Simulation Package (VASP) code [32,33]. The plane-wave basis-set is used to represent electronic wavefunctions with a cut-off energy of 400 eV. The pseudopotentials based on the projector augmented wave (PAW) method [34,35] explicitly include the Pb 5d, 6s, and 6p, the Ti 3s, 3p, 3d, and 4s, and the O 2s and 2p electrons as valence states. Spin polarization is considered for all calculations. Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid functional [30] is used for the description of the exchange-correlation energies, which includes in part the exact nonlocal exchange of Hartree-Fock theory into the Perdew-Burke-Ernzerhof functional (PBE) [17] of the GGA. The exchange potential is composed of 25% of the HF exchange and 75% of the PBE exchange as Heyd et al. suggested [30], while electronic correlation is represented by the PBE functional. A screening parameter for the semilocal PBE exchange and the screened nonlocal exchange is $0.2 \text{ \AA}^{-1}$.

The effectiveness and validity of the HSE06 hybrid functional was carefully tested and confirmed for ferroelectric PbTiO_3 by comparing

available exchange-correlation functionals in a recent paper [18]. For example, the band gap is evaluated as 1.62 eV using the LDA functional [18], which has been commonly used to investigate the atomic and electronic structure of PbTiO_3 in previous studies, but is less than half of the experimental value of 3.4 eV [29]. On the other hand, the band gap calculated by the HSE06 hybrid functional is 3.41 eV with extremely high accuracy (error less than 1%) [31].

In this study, we investigate the 180° domain walls with O-vacancies in ferroelectric PbTiO_3 . Figure 4.1 shows the simulation model. The 180° domain wall is the most stable in Pb-centered configuration [36]. A three-dimensional periodic boundary condition is applied in the plane-wave pseudopotential calculations, so that the supercell size along the x direction is six unit cells where undesirable interactions from the neighboring domain wall are sufficiently avoided. A vacancy, denoted as V_α^q ($\alpha = \text{O1}, \text{O2}$ and O3), is introduced by the removal of one corresponding atom from the simulation supercell. Here, the oxygens O1, O2 and O3, which are located in the polar [001], non-polar [010], and non-polar [100] directions relative to the Ti atom, respectively, are not equivalent to each other due to

the tetragonal symmetry and additional symmetry breaking due to the domain wall. q denotes the charge state of the vacancy and all possible charge states, $q=0-2+$ for the O1, O2 and O3 vacancies. The vacancy-vacancy interactions due to the three-dimensional periodic boundary condition can be ignored by the introduction of two or more unit cells along the y and z directions. Thus, the simulation cell dimensions in the x , y , and z directions were set to $6a$, $2a$, and $2c$, respectively, where a and c are the theoretical lattice constants of bulk PbTiO_3 , $a=3.876$ Å and $c=4.150$ Å. The Brillouin zone (BZ) integrations is carried out with a $1 \times 2 \times 2$ Monkhorst-Pack k -point mesh [37]. To obtain the structural ground state, the atomic configuration is fully relaxed using the conjugate gradient method until the Hellmann–Feynman forces are less than 0.01 eV/Å.

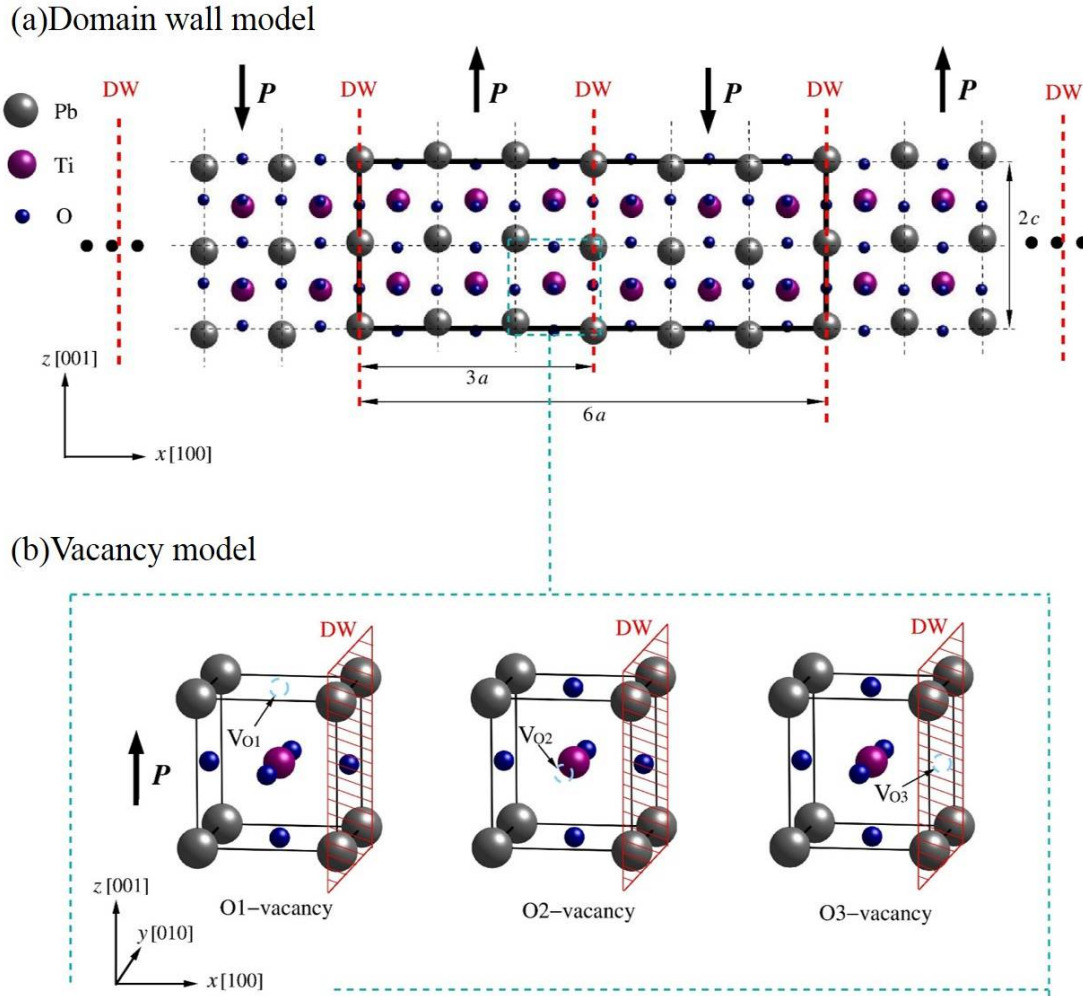


Fig.4.1 (a) Simulation models for 180° domain walls with O vacancies in PbTiO_3 . The solid box represents the simulation supercell. The arrows labeled $\mathbf{P}$ indicate the spontaneous polarization. (b) A vacancy, denoted as V_{O1} , V_{O2} and V_{O3} are introduced by the removal of one corresponding atom from the simulation supercell, respectively. The oxygens O1, O2 and O3 are located in the polar [001], non-polar [010], and non-polar [100] directions relative to the Ti atom, respectively.

4.3 Results and discussion

4.3.1 Energetic stability of O-vacancies on a 180° domain walls in PbTiO₃

We introduce the vacancy formation energy to investigate the energetic stability of vacancies on a 180° domain wall in PbTiO₃ and their charged states:

$$E_{\text{vf}}(V_{\alpha}^q) = [E_{\text{tot}}(V_{\alpha}^q) + \mu_{\alpha} + q(E_{\text{VBM}} + \varepsilon_{\text{F}})] - E_{\text{tot}}(\text{perfect}), \quad (2)$$

$E_{\text{tot}}(V_{\alpha}^q)$ is the total energy of a simulation model with a vacancy V_{α}^q . μ_{α} denotes the chemical potential of atom α in PbTiO₃, which has different value depending on the surrounding environment. A valid range of that of PbTiO₃ is determined from the thermodynamic equilibrium conditions and the requirement to prevent the formation of other solid solutions or secondary phases. In this study, the oxygen-poor and oxygen-rich conditions, where $\Delta\mu_{\text{O}} = -2.54$ eV and $\Delta\mu_{\text{O}} = 0$ eV respectively, are the main focus [31]. E_{VBM} is the valence band maximum (VBM) of PbTiO₃ with a potential alignment correction [26,38]. ε_{F} is the Fermi level measured from the VBM which vary from the VBM to the conduction band minimum (CBM). $E_{\text{tot}}^{(\text{perfect})}$ is the total energy of perfect (defect-free)

PbTiO₃.

Figure 4.2 shows the vacancy formation energies E_{vf} with respect to ε_{F} for O1, O2 and O3 vacancy around 180° domain wall under the oxygen-poor condition. The vacancy formation energies in bulk PbTiO₃ with each oxygen vacancy are shown for comparison. The charged O1-vacancies V_{O1}^+ and V_{O1}^{2+} have low and negative formation energies -0.73 eV and -3.88 eV at the VBM, respectively. This exhibits that the charged O1-vacancies can be formed around the 180° domain wall spontaneously under the condition that the Fermi level is near the VBM. On the other hand, the neutral O1-vacancy V_{O1}^0 has high and positive formation energy at 2.44 eV at the VBM, which indicates that the formation of the neutral O1-vacancy is hard even under oxygen-poor conditions. Moreover, the formation energy of V_{O1}^{2+} is the lowest at the VBM among them, which exhibits that the O1 vacancy is preferentially doubly ionize. This trend vary under the condition that the Fermi level is near the CBM, where the formation energies of O1-vacancies with different charged state are large and positive at approximately 2.7 eV. Thus O1 vacancy is unlikely to form near the CBM. These trends are nearly the

same in bulk PbTiO_3 with each oxygen-vacancy, but the value of the formation energy is different which is discussed later.

The tendency of the formation energy for O2 and O3 vacancies is similar to the O1 vacancies basically, whereas the value for O2 and O3 is slightly higher than that of the O1 vacancies. Thus, the position of oxygen-vacancy formed in ferroelectric material is highly influenced by the existence of 180° domain wall in crystal.

Figure 4.3 shows E_{vf} for V_{O1} , V_{O2} , and V_{O3} with respect to ϵ_{F} under oxygen-poor and oxygen-rich conditions. The vacancy formation energies in bulk PbTiO_3 , where V_{O2} and V_{O3} are similar due to the tetragonal symmetry, are also shown for comparison. We take the lowest formation energy among all the charge states for each vacancy at each Fermi level. As shown in fig.4.3 (a), the formation energies of O1, O2 and O3 vacancy in 180° domain wall are negative over a wide range of Fermi levels ($\epsilon_{\text{F}} < 1.7$ eV) under oxygen-poor condition, which exhibits that oxygen vacancies can be formed around 180° domain wall spontaneously during crystal growth. Moreover, the formation energies of O1, O2 and O3 in 180° domain wall are lower than those of the bulk over the entire range of Fermi

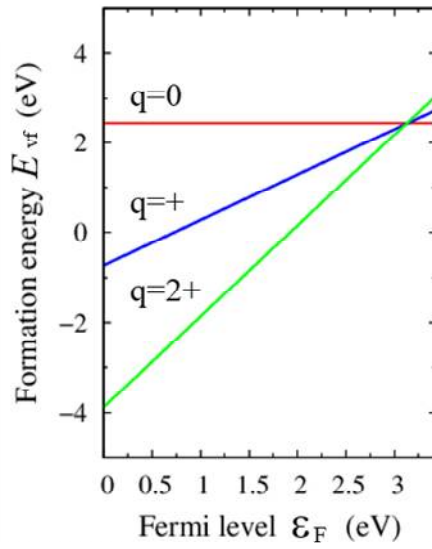
levels, which exhibits that oxygen vacancies in PbTiO_3 are formed more easily near a 180° domain wall than in the bulk. To date, there have been several reports on the presence of O-vacancies inside the domain walls in ferroelectric PbTiO_3 , which indicates the validity of these results. On the other hand, the formation energies of O1, O2 and O3 vacancy significantly increase under oxygen-rich condition, so that the stability ranges of V_{O1} , V_{O2} and V_{O3} are restricted within the narrow range at $\epsilon_F < 0.4$ eV. Thus, O1, O2 and O3 vacancies become less stable under the oxygen-rich condition.

Figure 4.4 shows the charge transition levels for each vacancy at the 180° domain wall in ferroelectric PbTiO_3 . The defect-transition level corresponds to the intersection of the vacancy formation energies for the different charge states [see also Fig. 4.2]. The results of vacancies in bulk PbTiO_3 are also shown for comparison. For O1 vacancy, there is a $2+/+0$ transition level at 0.3 eV below the CBM. Here, the range of Fermi energy where the formation energy of V_{O1}^+ is the lowest is very narrow, so that V_{O1} behaves as a double shallow donor that releases two electrons. Similarly, for O2 and O3 vacancy, there are a $2+/0$ transition level at 0.5 eV and 0.3 eV below the CBM, respectively. Thus, V_{O2} and V_{O3} also act as double

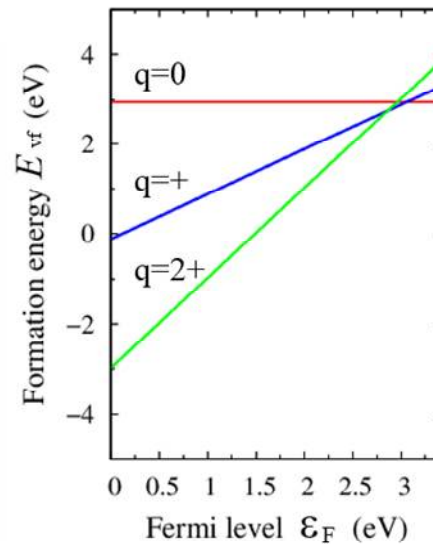
shallow donors. Furthermore, the transition level of an O-vacancy in the domain wall is closer to the CBM than that of O-vacancy in the bulk. This indicates that an O-vacancy in the 180° domain wall contributes to the conductivity preferentially than in the bulk.

(a) O1-vacancy

180° domain wall

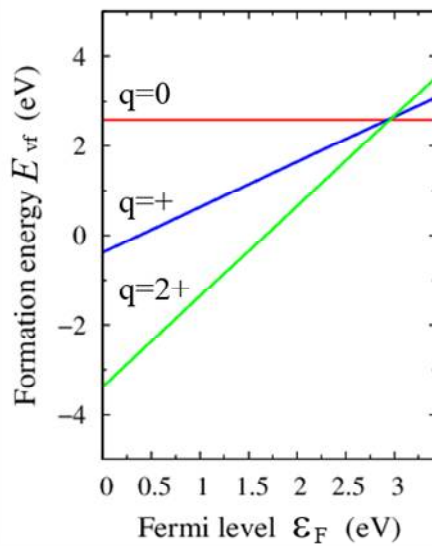


Inside(Bulk)

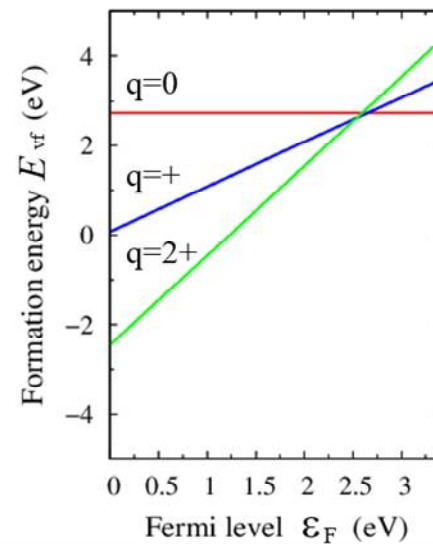


(b) O2-vacancy

180° domain wall

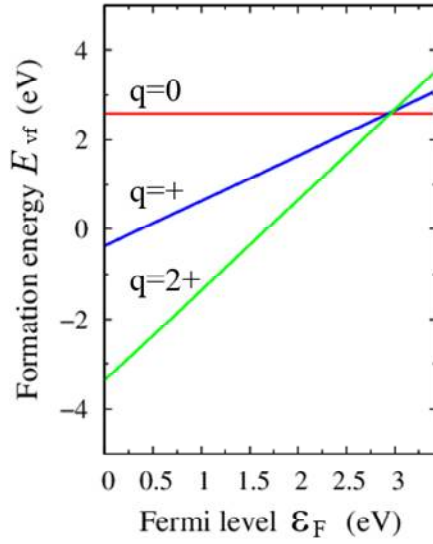


Bulk



(c) O3-vacancy

180° domain wall



Bulk

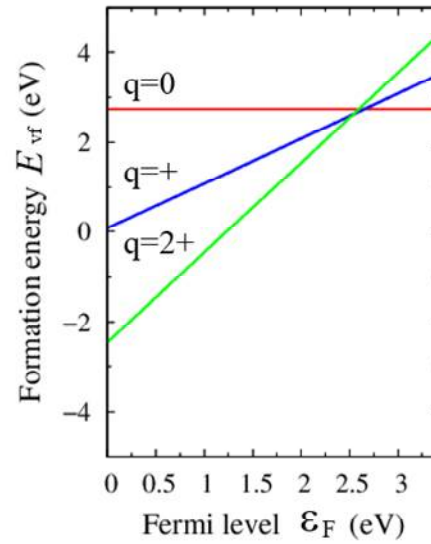


Fig.4.2 Vacancy formation energies E_{vf} , of V_{O1} , V_{O2} and V_{O3} at a 180° domain wall as a function of the Fermi level ϵ_F , under an O-poor limit. q on each line indicates the charge state. The vacancy formation energies in bulk PbTiO_3 with each oxygen vacancy are shown for comparison.

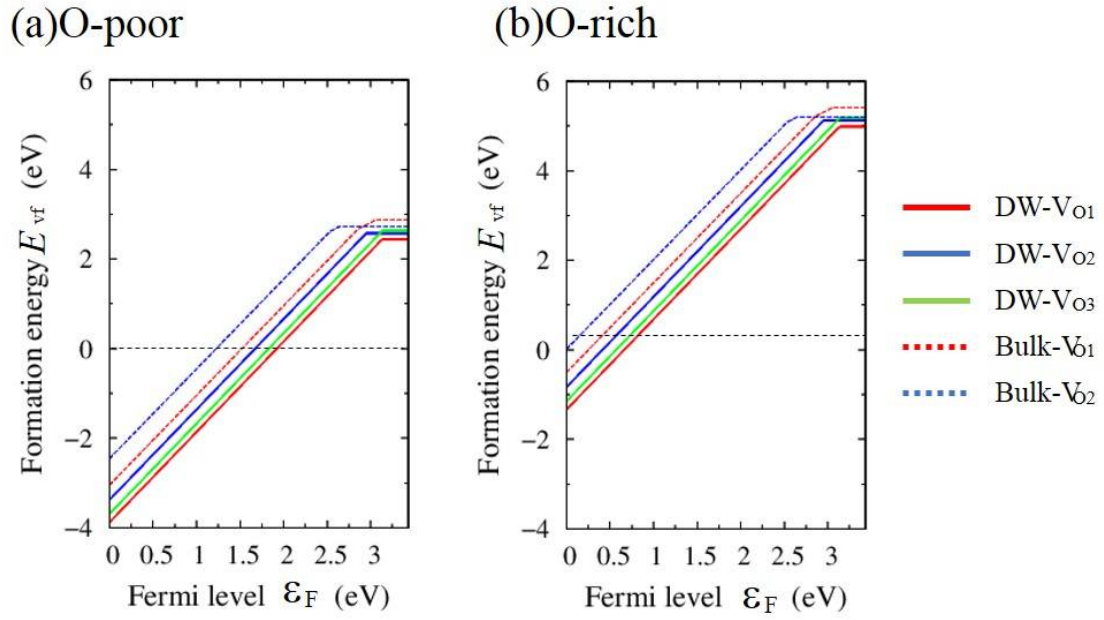


Fig. 4.3 Vacancy formation energies E_{vf} of V_{O1} , V_{O2} and V_{O3} at a 180° domain wall and inside the bulk in PbTiO_3 as a function of the Fermi level ϵ_F , under (a) the O-poor limit and (b) the O-rich limit.

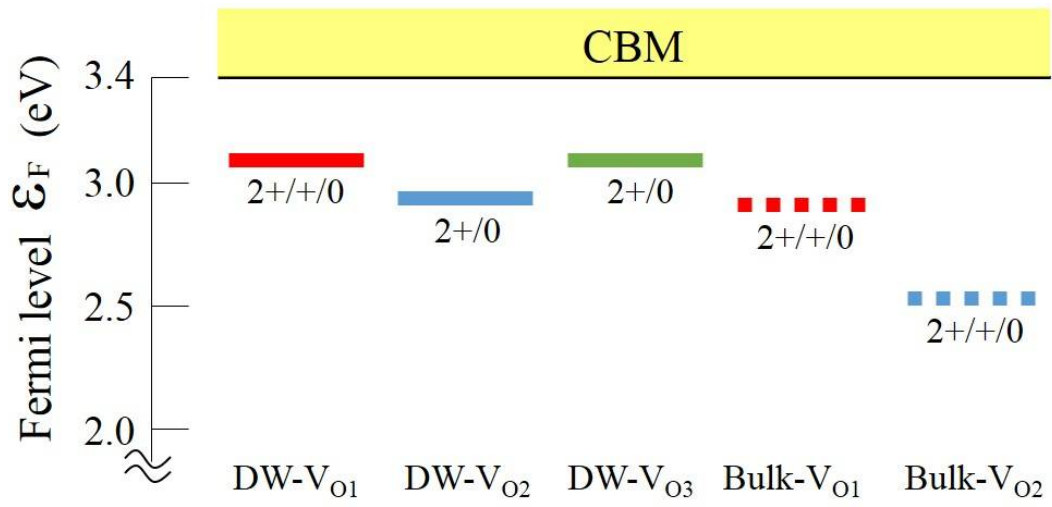


Fig. 4.4 Defect transition levels of V_{O1} , V_{O2} and V_{O3} at the 180° domain wall and inside the bulk in PbTiO_3 . Numbers on each transition level line indicate the charge of charge state, q .

4.3.2 Polarization pattern of a 180° domain walls with O-vacancies in ferroelectric PbTiO_3

For understanding the influence of vacancies on the ferroelectricity of a 180° domain wall in PbTiO_3 , we introduce a site-by-site local polarization P [39-45], which can be evaluated by equation (1) as shown in Chapter 2. The local polarization is evaluated for each local unit cell, and defined for each centered atom, as illustrated in Fig. 4.5. Weights are set according to the number of unit cells that share atom j , e.g., $w_{\text{Pb}} = 1$, $w_{\text{Ti}} = 1/8$ and $w_{\text{O}} = 1/4$ for the Pb-centered local unit cell.

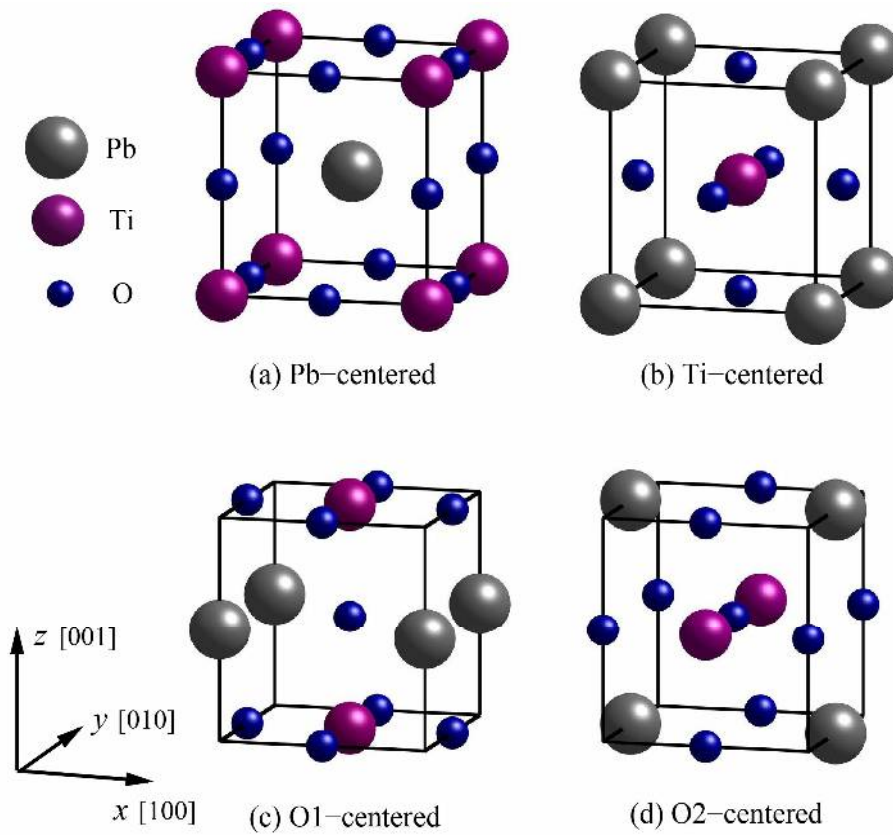


Fig.4.5 Definition of (a) Pb-, (b) Ti-, (c) O1-, and (d) O2-centered local unit cells in PbTiO_3 for the evaluation of local polarization via Eq. (1) as shown in Chapter 2.

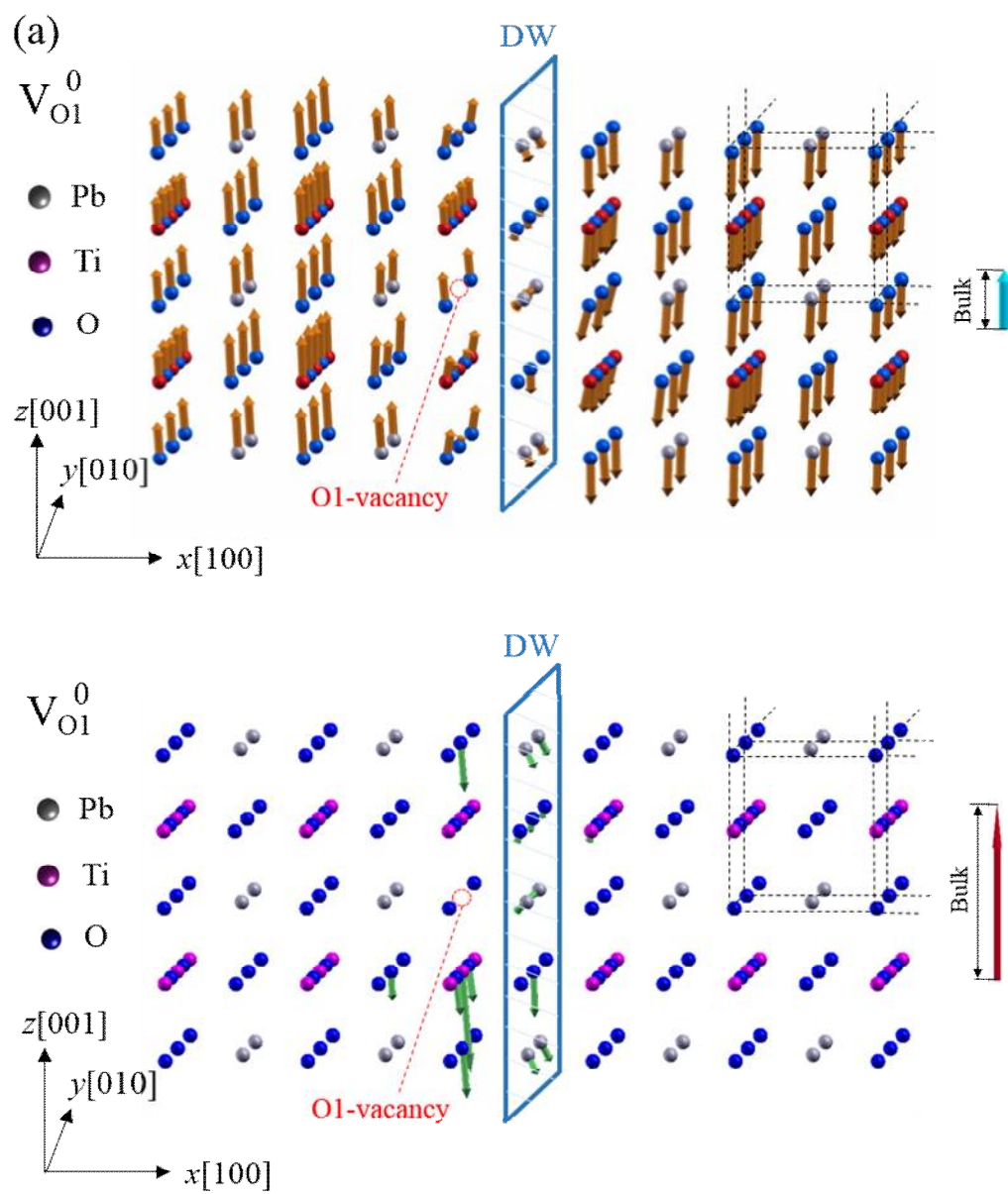
Figure 4.6(a) shows the local polarization distribution around a 180° domain wall with V_{O1}^0 in ferroelectric PbTiO_3 . We calculate the local polarization in each atom centered unit cell as shown in Fig.4.5 and represent the polarization magnitude and direction by an arrow from the atom. The yellow and green arrows indicate the local polarization and the polarization difference from a perfect (defect-free) 180° domain wall in PbTiO_3 , respectively, at the upper and lower side in Fig.4.6(a). The blue and red arrows indicate spontaneous polarization in the bulk, which their arrow length is different at the upper and lower side to explain the result clearly. And the local polarization distribution in a 180° domain wall with no vacancy in ferroelectric PbTiO_3 , where the polarization direction changes from upward on the one side to downward on the other and there is no polarization at the center of the domain wall, is shown in Fig.4.6 (c) for comparison.

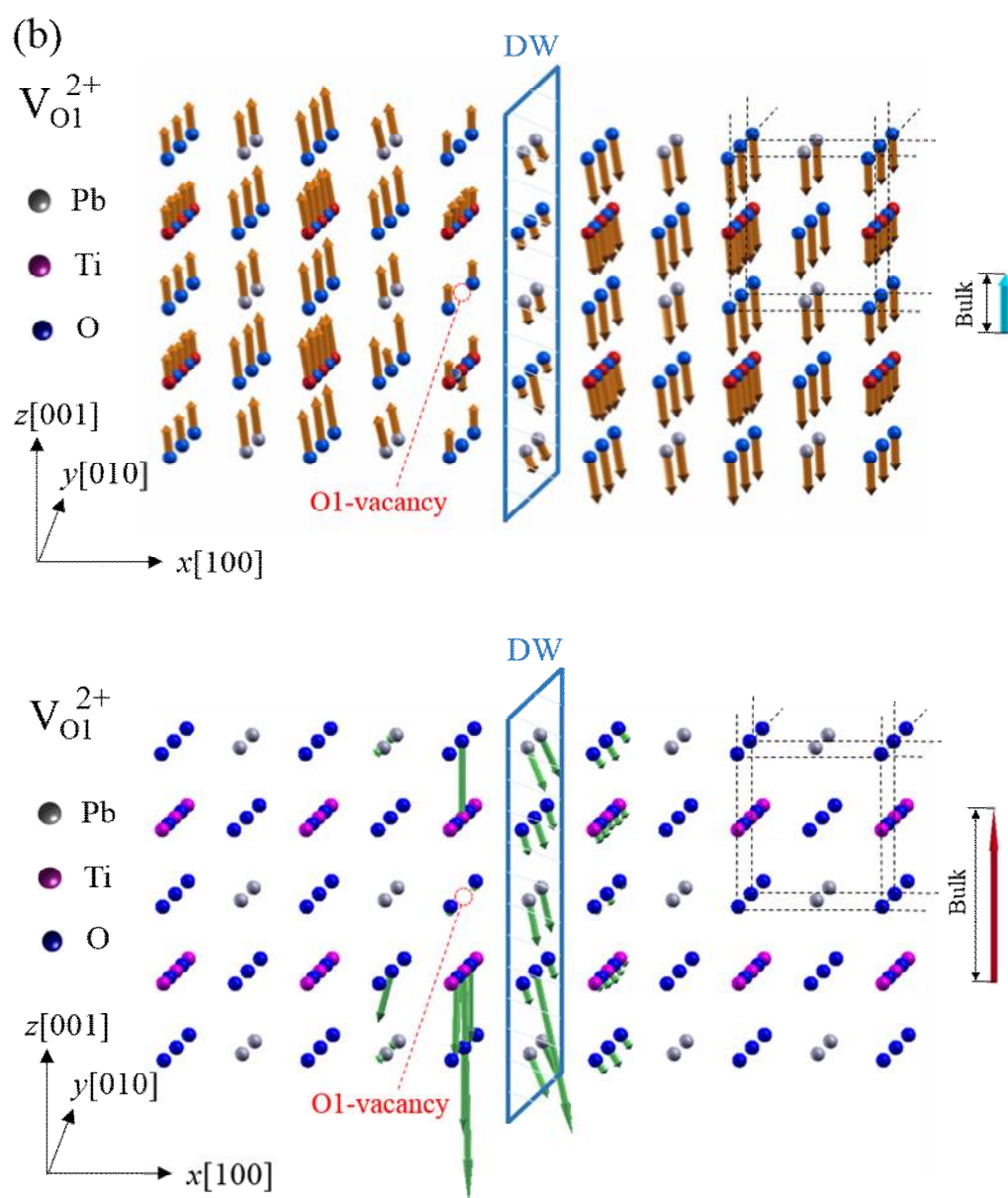
The polarization distribution around the O1-vacancy inside the 180° domain wall is highly disturbed, which originates from the high interaction between the O1-vacancy and the 180° domain wall. The change in polarization around V_{O1} in front of the domain wall is highly confined and

the direction is almost $[00\bar{1}]$, which is the same tendency of that around V_{O1} in bulk PbTiO_3 . Similar polarization directed to $[00\bar{1}]$ is also evident only at the center of the domain wall. These results indicate that the presence of V_{O1} suppresses ferroelectricity around the vacancy in front of the domain wall, where the left side of the domain wall, and induces ferroelectricity only at the center of domain wall. Thus, an O1-vacancy around a 180° domain wall in PbTiO_3 causes a shift of the domain wall towards the vacancy and pinning of the domain wall, which corresponds to the previous theoretical study. This effect is significantly enhanced when the O1 vacancy is $2+$ charged [see also Fig.4.6(b)]. The change of polarization immediately around V_{O1}^{2+} is particularly large, so that the local polarization in front of the domain wall becomes almost zero.

Figure 4.7 shows the local polarization distribution in 180° domain walls with (a) V_{O1}^{2+} , (b) V_{O2}^{2+} , and (c) V_{O3}^{2+} in PbTiO_3 . The local polarization distribution in bulk PbTiO_3 with polarization along z direction, which include V_{O1}^{2+} and V_{O2}^{2+} , is also indicated on the lower side in each figure for comparison. Green arrows indicate the local polarization difference from the perfect (defect-free) 180° domain wall and the bulk in

PbTiO₃. In contrast to the O1-vacancy, O2- and O3-vacancies induce polarization perpendicular to the [010] axis and outward from V_{O2}^{2+} . Thus, the effect of the O-vacancy on the polarization distribution in a 180° domain wall is completely different depending on the position of the O-vacancy with respect to the domain wall. Furthermore, the magnitude of change in the polarization of the 180° domain wall is larger than that in the bulk. In particular, the range of the effect of the O1-vacancy is not only around the O1-vacancy, but also across the 180° domain wall. Thus, the effect of the O-vacancy on the polarization distribution in a 180° domain wall is stronger than that in the bulk, which is due to the strong interaction between the domain wall and O-vacancy.





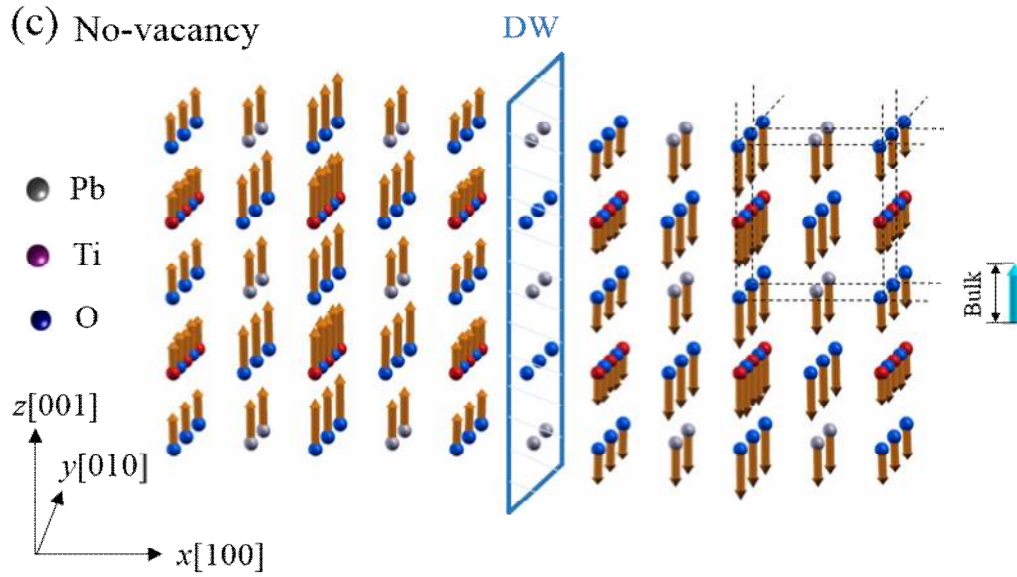
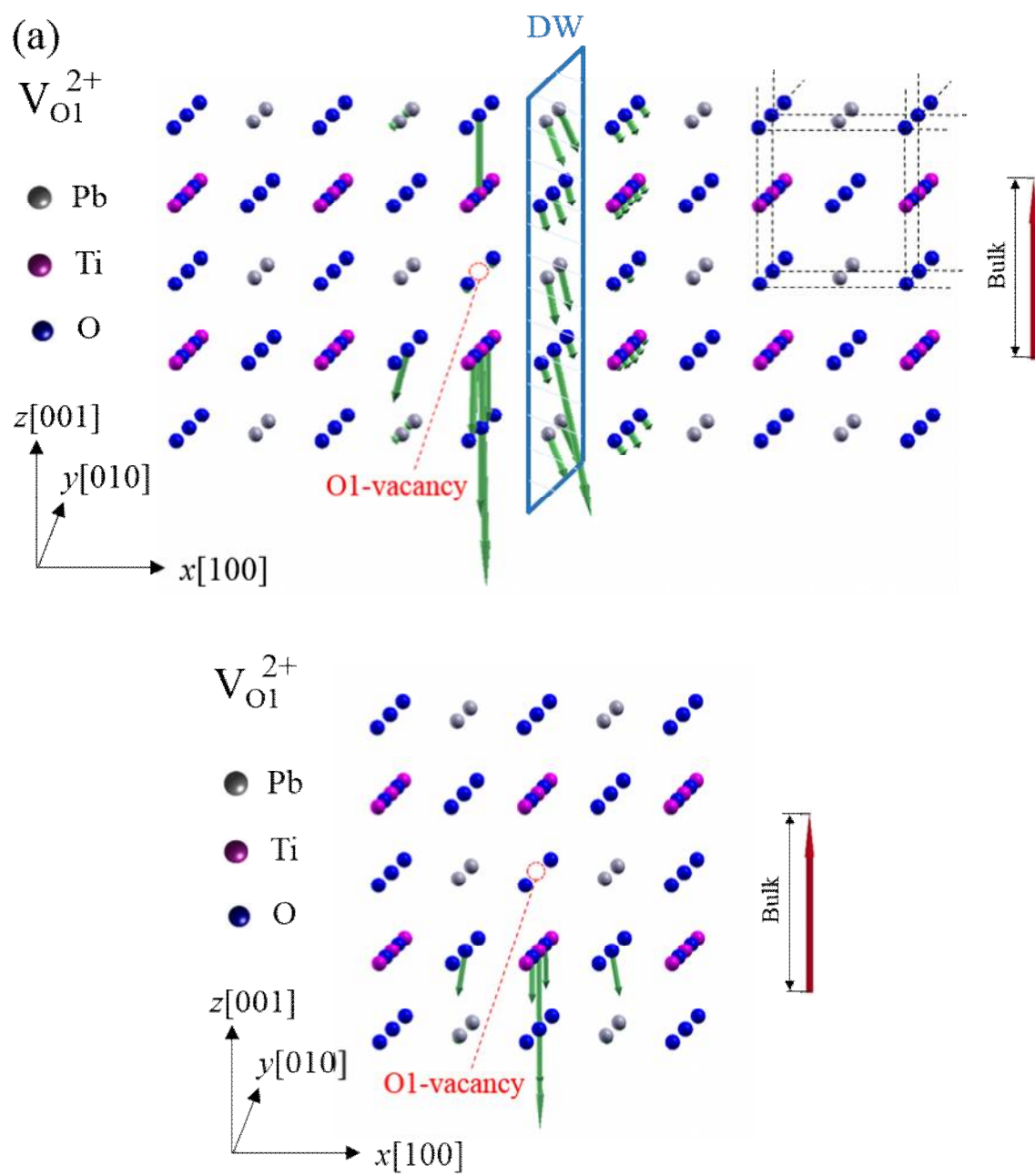
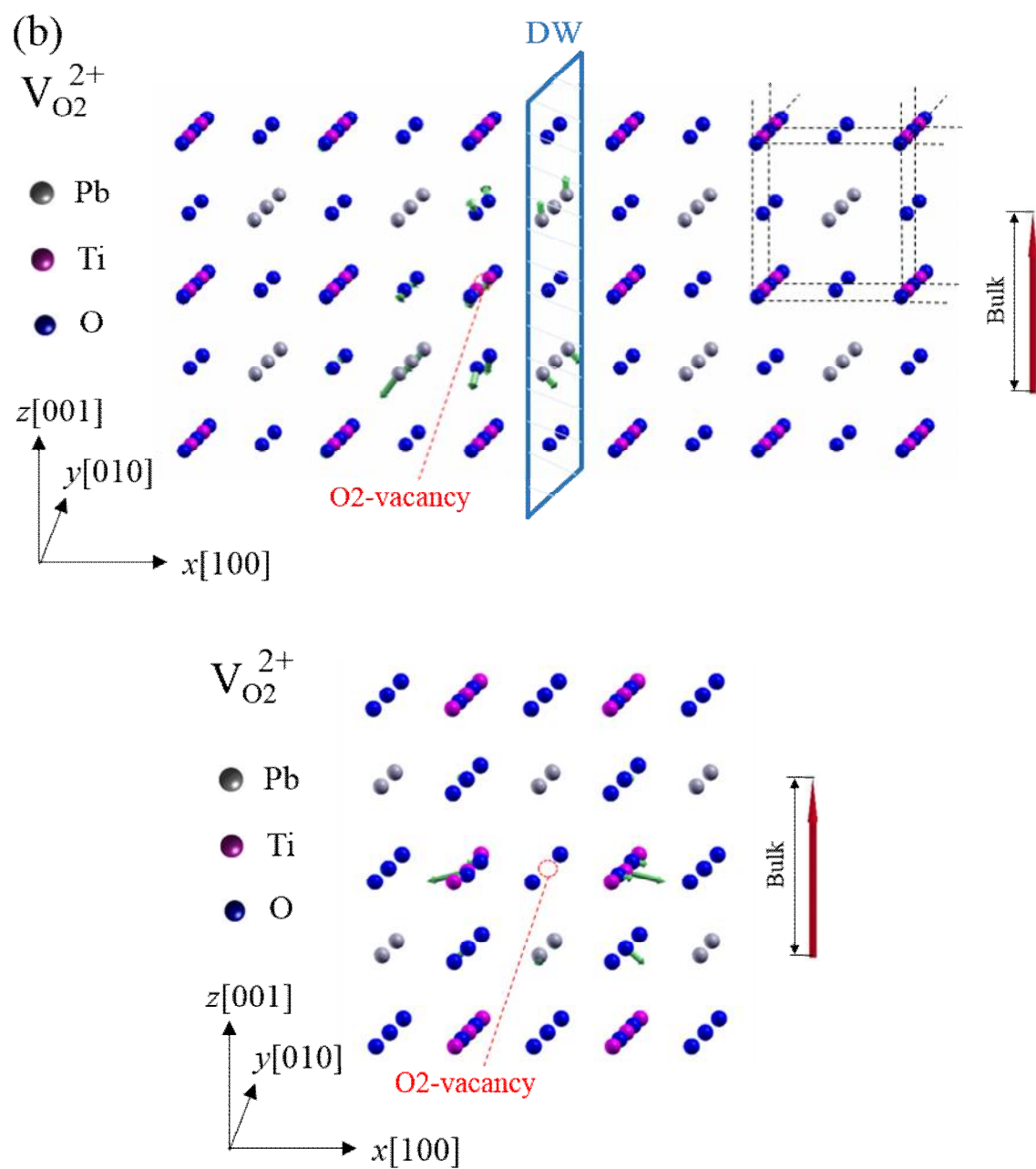


Fig.4.6 Local polarization distribution in a 180° domain wall with (a) V_{O1}^0 and (b) V_{O1}^{2+} in $PbTiO_3$. The yellow and green arrows indicate the local polarization and the local polarization difference from that of a perfect (defect-free) 180° domain wall, respectively. The blue and red arrows indicate spontaneous polarization in the bulk. And the local polarization distribution in a 180° domain wall with no vacancy in ferroelectric $PbTiO_3$ is also shown in Fig. 4.6 (c) for comparison.





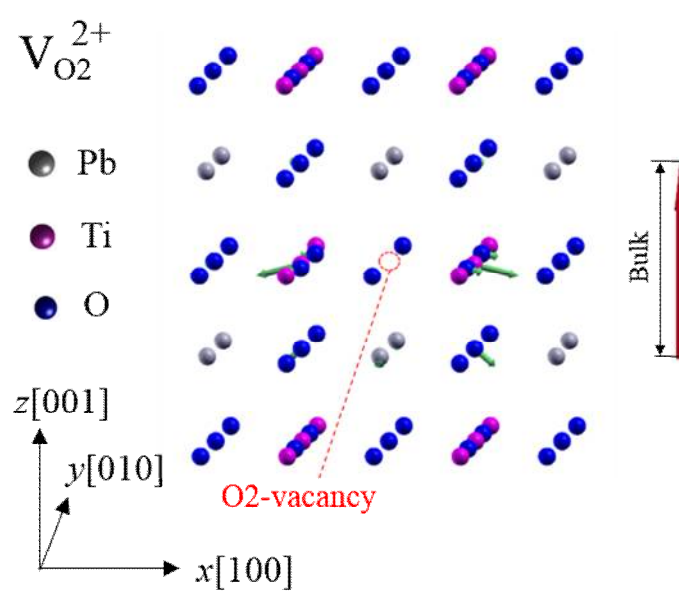
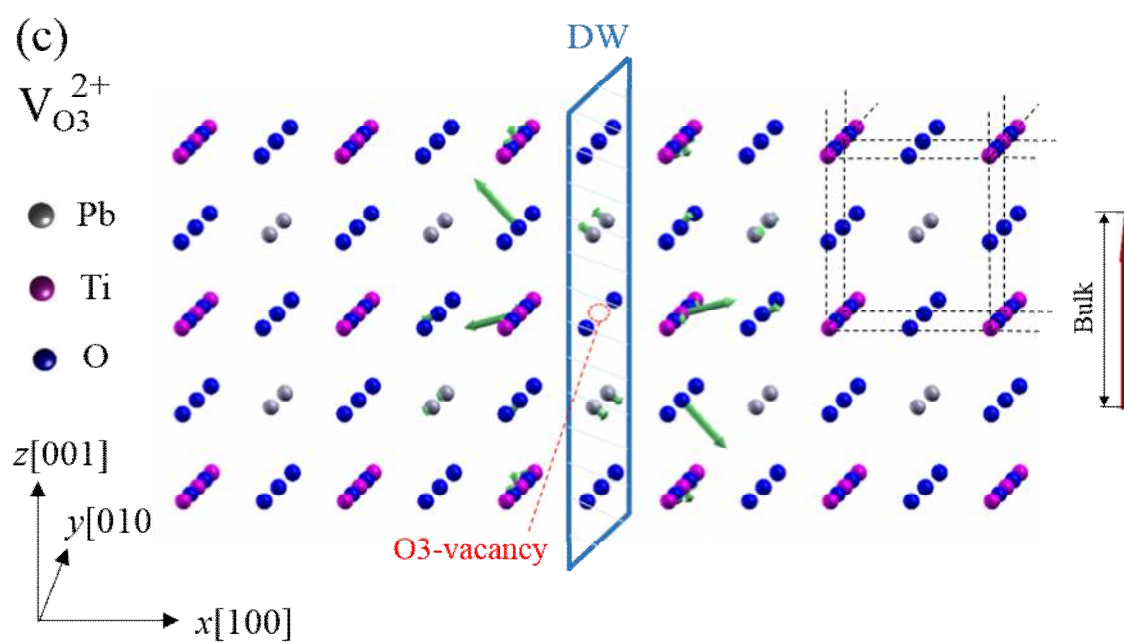


Fig. 4.7 Local polarization distribution in a 180° domain wall with (a) V_{O1}^{2+} and (b) V_{O2}^{2+} and (c) V_{O3}^{2+} in $PbTiO_3$. The local polarization distributions in the bulk with V_{O1}^{2+} and V_{O2}^{2+} are also indicated on the lower side of each figure for comparison. The green arrows indicate the local polarization difference from that of a perfect (defect-free) 180° domain wall. Red arrows indicate spontaneous polarization in the bulk.

4.4 Conclusions

We investigated the ferroelectricity in 180° domain walls with O-vacancies in PbTiO_3 . From an energetic view, an O-vacancy is more likely to form inside a 180° domain wall than inside the bulk over a wide range of Fermi-energy under oxygen-poor conditions, where the vacancy acts as a double shallow donor and contributes to the conductivity preferentially than that inside the bulk.

The defect interaction between the 180° domain wall and O-vacancy strongly influences the polarization distribution in PbTiO_3 , and the effect is completely different depending on the location of the O-vacancy with respect to the domain wall. An O-vacancy that is located in the polar $[001]$ direction relative to the Ti atom suppresses ferroelectricity around the vacancy in front of the domain wall, and enhances ferroelectricity only at the center of domain wall, which leads to a shift of the domain wall towards the vacancy and pinning of the domain wall. On the other hand, an O-vacancy that is located in the non-polar $[100]$ and $[010]$ directions relative to the Ti atom induces polarization perpendicular to the $[010]$ axis and outward from the vacancy. Furthermore, the

magnitude of the polarization change around an O-vacancy inside the 180° domain wall is larger than that inside the bulk, due to the strong interaction between the 180° domain wall and O-vacancy.

References

- [1] W. L. Warren, D. Dimos and R. M. Waser, *MRS Bull.* **21** 40 (1996).
- [2] J. F. Scott and M. Dawber, *Applied Physics Letters* **76** 3801 (2000).
- [3] W. L. Warren, H. N. Al-Shareef, D. Dimos, B. A. Tuttle and G. E. Pike, *Applied Physics Letters* **68** 1681 (1996).
- [4] S. Pöykkö S and D. J. Chadi, *Physical Review Letters* **83** 1231 (1999).
- [5] L. He and D. Vanderbilt, *Physical Review B* **68** 134103 (2003).
- [6] X. Du and I. Wei Chen, *Journal of Applied Physics* **83** 7789 (1998).
- [7] G. Burns and B. A. Scott, *Physical Review Letters* **25** 1191 (1970).
- [8] X. Du and I. W. Chen, *Journal of Applied Physics* **83** 7789 (1998).
- [9] R. E. Cohen, *Nature (London)* **358** 136 (1992).
- [10] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata and M. Sakata, *Physical Review Letters* **87** 217601 (2001).
- [11] R. Resta, M. Posternak and A. Baldereschi, *Physical Review Letters* **70** 1010 (1993).
- [12] W. Zhong, R. D. King-Smith and D. Vanderbilt, *Physical Review Letters*, **72** 3618 (1994).
- [13] P. Hohenberg and W. Kohn, *Physical Review* **136** B864 (1964).

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- [14] W. Kohn and L. Sham, *Physical Review* **140** A1133 (1995).
- [15] D. M. Ceperley and B. J. Alder, *Physical Review Letters* **45** 566 (1980).
- [16] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais *Physical Review B* **46** 6671 (1992).
- [17] J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters* **77** 3865 (1996).
- [18] T. Shimada, X. Wang, S. Tomoda, P. Marton, C. Elsässer and T. Kitamura *Physical Review B* **83** 094121 (2011).
- [19] C. H. Park and D. J. Chadi *Physical Review B* **57** 13961 (1998).
- [20] S. Pöykkö and D. J. Chadi *Physical Review Letters* **83** 1231 (1999).
- [21] S. Pöykkö and D. J. Chadi *Applied Physics Letters* **76** 499 (2000).
- [22] Z. Zhang, P. Wu, L. Lu and C. Shu *Applied Physics Letters* **88** 142902 (2006).
- [23] P. Erhart, R. –A. Eichel, P. Träskelin and K. Albe *Physical Review B* **76**, 174116 (2007).
- [24] Z. Alahmed and H. Fu, *Physical Review B* **76** 224101 (2007).
- [25] Z. Zhang, P. Wu, L. Lu and C. Shu *Journal of Alloys and Compounds*

449 362 (2008).

[26] Y. Yao and H. Fu *Physical Review B* **84** 064112 (2011).

[27] T. Shimada, Y. Uratani and T. Kitamura *Applied Physics Letters* **100** 162901 (2011).

[28] T. Shimada, Y. Uratani and T. Kitamura *Acta Materialia* **60** 6322 (2012).

[29] J. Robertson, W. L. Warren and B. A. Tuttle *Journal of Applied Physics* **77** 3975 (1995).

[30] J. Heyd, G. E. Scuseria and M. Ernzerhof *Journal of Chemical Physics* **118** 8207 (2003); **124** 219906 (2006).

[31] T. Shimada, T. Ueda, J. Wang and T. Kitamura *Physical Review B* **87** 174111 (2013).

[32] G. Kresse and J. Hafner *Physical Review B* **47** 558 (1993).

[33] G. Kresse and J. Furthmüller *Physical Review B* **54** 11169 (1996).

[34] P. E. Blöchl, *Physical Review B* **50** 17953 (1996).

[35] G. Kresse and D. Joubert *Physical Review B* **59** 1758 (1999).

[36] R. K. Behera et al, *Journal of Physics Condensed Matter* **23** 175902 (2011).

- [37] H. J. Monkhorst and J. D. Pack, *Physical Review B* **13** 5188 (1976).
- [38] M. Choi, F. Oba and I. Tanaka, *Physical Review B* **78** 014115 (2008).
- [39] T. Shimada, Y. Umeno and T. Kitamura, *Physical Review B* **77** 094105 (2008).
- [40] T. Shimada, S. Tomoda and T. Kitamura, *Physical Review B* **81** 144116 (2011).
- [41] B. Meyer and D. Vanderbilt, *Physical Review B* **65** 104111 (2002).
- [42] T. Shimada, S. Tomoda and T. Kitamura, *Journal of Physics Condensed Matter*, **22** 355901 (2010).
- [43] T. Shimada, X. Wang, Y. Kondo and T. Kitamura, *Physical Review Letters* **108** 067601 (2012).
- [44] G. Pilania and R. Ramprasad, *Physical Review B* **82** 155442 (2010).
- [45] T. Shimada, S. Tomoda and T. Kitamura, *Physical Review B* **79** 024102 (2009).

Chapter 5 Conclusion

In this thesis, I have precisely investigated the polarization pattern derived from the surface and internal structures in ferroelectric nanofilms from the atomistic and electronic points of view using the first principle calculations.

In Chapter 2, as the most common surface structure, we have investigated the flat (001) surface with polarization perpendicular to surface in PbTiO_3 nanofilms. While the gradually enhanced and decreased polarization pattern is observed due to the surface termination in nanofilm with polarization parallel to (001) surface, which is studied by Umeno et.al, the polydomain structure is formed and the polarization is rotated at the junction between surface and domain wall in nanofilms with polarization perpendicular to (001) surface. This polydomain structure, which is generally called closure domain structure, is energetically favorable than the paraelectric structure even in the thinnest, one unit-cell thick film without screening effect of electrode, which indicates that no critical thickness for ferroelectricity intrinsically exists. Additionally, by the further analysis from the atomic and electronic structure, it is revealed that the

closure domain structure is produced by the in-plane atomic displacement in the surface layer, and consists of both the 180° and 90° domain wall.

In Chapter 3, PbTiO_3 surface step consisting of (100) and (001) flat surfaces is investigated. In surface step with polarization along [010] direction, not only the polarization along [010] direction is locally enhanced and decreased due to the surface termination as in flat (001) surface with polarization parallel to surface, but also the polarization along [001] direction is emerged. Additionally, a compressive strain along [010] direction decreases ferroelectricity, and spontaneous polarization rotates from the [010] direction to the [001] direction at a critical strain. Simultaneously, the surface step is divided into domains along the step, which indicates that domain wall is induced along the surface step in ferroelectric nanofilms with surface step. On the other hand, in the case of the surface step with polarization along [100] direction which is investigated by my coworker Wang et.al, polarization along [100] direction is suppressed and polarization along [001] direction is emerged due to the screening of surface polarization charge.

In Chapter 4, we investigated the ferroelectricity of 180° domain walls

with oxygen-vacancies in PbTiO_3 . An O-vacancy that is located in the polar [001] direction relative to the Ti atom suppresses ferroelectricity around the vacancy in front of the domain wall, and enhances ferroelectricity only at the center of domain wall, which leads to a shift of the domain wall towards the vacancy. Hence, we can guess that the domain wall in ferroelectric nanofilms is formed at oxygen vacancy by preference. On the other hand, an O-vacancy that is located in the non-polar [100] and [010] directions relative to the Ti atom induces polarization perpendicular to the [010] axis and outward from the vacancy.

Thus, the surface and internal structures strongly affect the ferroelectricity of PbTiO_3 nanofilms. We will investigate the further complex effect for ferroelectricity in the future.

List of Publications

Full Length Papers and Letters

1. “Ab initio study of ferroelectricity in edged PbTiO_3 nanowires under axial tension”

Takahiro SHIMADA, Shogo TOMODA, and Takayuki KITAMURA
Physical Review B, Vol. 79, art.024102 (2009).

2. “Ab initio study of ferroelectric closure domains in ultrathin PbTiO_3 films”

Takahiro SHIMADA, Shogo TOMODA, and Takayuki KITAMURA
Physical Review B, Vol. 81, art.144116 (2010). (in Chapter 2)

3. “First-principles study on ferroelectricity at PbTiO_3 surface steps”

Takahiro SHIMADA, Shogo TOMODA, and Takayuki KITAMURA
Journal of Physics Condensed Matter, Vol. 22, art.355901 (2010).
(in Chapter 3)

4. “Coexistence of rectilinear and vortex polarizations at twist boundaries in ferroelectric PbTiO_3 from first principles”

Takahiro Shimada, Xiaoyuan Wang, Shogo Tomoda, Pavel Marton,
Christian Elsässer, and Takayuki Kitamura

Physical Review B, Vol. 83, art. 094121 (2011).

5. “Local suppression of ferroelectricity at PbTiO_3 surface steps: a density functional theory study”

Xiaoyuan WANG, Shogo TOMODA, Takahiro SHIMADA, Takayuki KITAMURA

Journal of Physics Condensed Matter, Vol.24, art.045903 (2012).

6. “Ferroelectricity at a junction structure of a 180° domain wall and a (001) surface in PbTiO_3 : A density functional theory study

Xiaoyuan WANG, Shogo TOMODA, Takahiro SHIMADA, Takayuki KITAMURA

Physica B, Vol.410, 22 (2013).

7. “Hybrid functional study on the ferroelectricity of domain walls with O-vacancies in PbTiO_3 ”

Shogo TOMODA, Takahiro SHIMADA, Taku UEDA, Jie WANG, and Takayuki KITAMURA

Mechanical Engineering Journal, Vol. 2, No. 3 (2015). (in Chapter 4)

International Conferences

1. “Ab initio study of critical thickness and closure domain structure in free-standing ultrathin PbTiO_3 films”

Shogo TOMODA, Takahiro SHIMADA, and Takayuki KITAMURA

Asian Conference on Mechanics of Functional Materials and Structures (ACMFMS 2014), (Nara, Japan, 2014.10)

Domestic Conferences

1. “Ab initio study of ferroelectricity in edged PbTiO_3 nanowires under axial tension”

Shogo TOMODA, Takahiro SHIMADA, and Takayuki KITAMURA

The Japan Society of Mechanical Engineers: M&M 2008 Materials and Mechanics Conference, (Ritsumeikan University, 2008.9)

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