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Origins of Conduction at Domain Boundaries, $LaAlO_3/SrTiO_3$ and Surface for Depolarization & Size Effect

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***Abstract*— The conductions at domain boundaries due to ferroelectric polarization and $LaAlO_3/SrTiO_3$ found by Ohtomo and Hwang [Nature 427, 423 (2004)] are intriguing. If these conductions are different from the conventional conductions at domain boundaries and oxide interfaces due to defects, they prove the earlier predictions [Phys. Rev. Lett. 86, 332(2001); Phys. Rev. B57, 789(1998)]. That is, when these conductions are primarily due to ferroelectric polarization as predicted, the foundations of mesoscale and nanoscale ferroelectrics should change. Considering conventional mechanisms including the high field effect as in the resistance switching (RRAM), we examine their origin and discuss these implications.**

Keywords—conduction; ferroelectric; interface; domain;2D electron; RRAM; electron layer; nano

I. INTRODUCTION

The carrier layers at insulator interfaces such as $SrTiO_3/LaAlO_3$ found in 2004 [1], domain boundaries [2-4], and surface of ferroelectrics (Fig.1) are intriguing topics. If and only if these carrier layers are primarily due to polarization discontinuity, i.e., ferroelectric polarization P_S as predicted and partly demonstrated in 2001 [5, 6], they have fundamental impacts on the basis of ferroelectricity. The examples are super-relaxation of size effect and domain configuration [5-7].

Although the predictions of Fig. 1 were confirmed by *ab initio* calculations [8, 9], the experimental results [1-5,10,11] can be due to conventional mechanisms, as evidenced in the failure of formation of both electron e^- and hole h^+ layer at the same locations by low field. Here, conduction originating from defects at domain boundaries [12-15] and the interfaces of heterostructures [16-18] and in bulk [19-25] have been established. High-field induced defects are also known [26, 27] in the studies of resistance switching. Therefore, we need to examine these experimental results without relying on theories.

II. INSULATIVITY AND SIZE EFFECT

Good ferroelectrics are good insulators without defects. This is because the conductance σ of ferroelectrics degrades their dielectric and ferroelectric response: σ adds a large imaginary part of dielectric constant $\varepsilon_i = \sigma/2\pi f\varepsilon_0$ where f and ε_0 are frequency and vacuum permittivity, respectively. Similarly, defects yields large ε_i and apparent real part of dielectric constant. Also, the switching of P_S is hindered by σ.

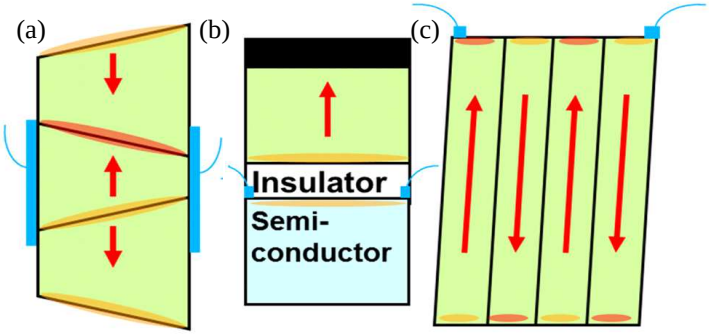

Fig. 1 Typical situations of free carrier layers by *polar discontinuity* i.e., *ferroelectric field effect*, where arrows and shades show P_S of ferroelectric and carrier layer, respectively (adopted from Phys. Rev. Lett. 86, 332 (2001) [5]): (a) head-to-head or tail-to-tail domain boundaries, (b) ferroelectric/insulator interface, whereas this figure expresses ferroelectric/insulator in the limit of the infinite thickness of the insulator layer in the middle, (c) clean damage-free surface, where vacuum be an ideal insulator. (b) and (c) were predicted [6]. (c) was experimentally verified in ref. [5,7]. These experiments and the theory [5,6] leaded to the generalization that includes (a). The theoretical calculation [5, 7, 37] showed the thickness of the layer was approximately 1~3 nm, which was later experimentally confirmed by $SrTiO_3/LaAlO_3$ [1].

Therefore, theories should treat ideal ferroelectrics as defect-free insulators, when they consider the fundamental ferroelectric properties.

By regarding ferroelectric as an ideal insulator, Batra et al. [28] predicted the inexistence of thin single-domain ferroelectric for the incomplete screening of the depolarization field, i.e., the field from P_S. *This initiated the "size effect by depolarization field", which is considered established.* Likewise, the depolarization field imposes strict restriction on the width of parallel domain, i.e., 180° or *cc* domains, which are vortex domain in the classical Kittel model [29].

The applications of this approach predict unconditional instabilities of ferroelectricity in almost any single-domain thin ferroelectric [30-32]. In particular, nanodomains (~3nm) were predicted to form abruptly for $l_d > 1.25\varepsilon_d$ nm (Fig. 2, l_d: separation between electrode and ferroelectric, ε_d: its relative permittivity) [31]. This disagrees with partial experimental successes of ferroelectric FET's, because typical ferroelectric FET has SiO_2-equivalent insulator thickness (l_d) of 10nm and the ferroelectric thickness of 300 nm and uses ferroelectric less resistive to the depolarization field instability than $PbTiO_3$.

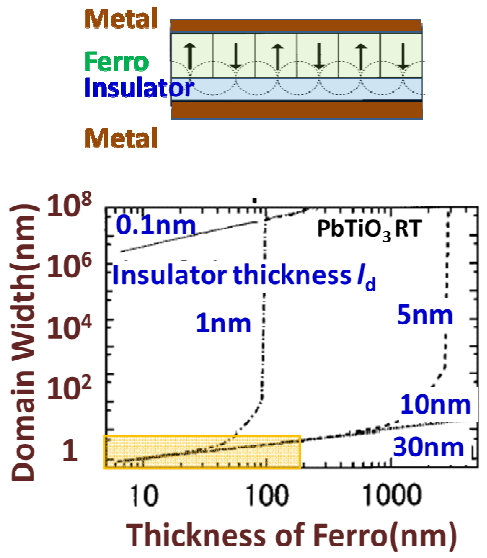

Fig. 2 Domain size vs. thickness of ferroelectric for different SiO_2 (ε_d = 3.9) thickness l_d, where the total free energy is minimized in the structure shown in the sketch (adopted from J. Appl. Phys. 83, 2179 (1998) [31]). $PbTiO_3$ was used in this calculations, because was one of the ferroelectrics that were practical and the most resistive to the depolarization field instability. In the orange shaded region, free energy calculations show that ferroelectricity disappears at RT for $l_d \geq 1.25\varepsilon_d$ nm. The compulsory nanodomain formation means that large domains for memory are absolutely not allowed, which seems to contradict with experiments. Therefore, this paper concluded that one of the basic assumptions, i.e., perfect insulativity with an infinite band gap was incorrect, although this prediction was later used for the explanation of fatigue by Bratkovsky and Levanyuk [34].

Moreover, even with nanodomains and $PbTiO_3$ -- depolarization-field-resistive --, ferroelectricity itself becomes unstable for practical range of parameters (orange shade in Fig. 2). Its unphysicalness was unnoticed [34], when only the fatigue in capacitors was studied. Another cause of the unawareness can be an inappropriate permittivity, i.e. the use of background permittivity for depolarization field [35], while it should be unity in practical cases [31-33].

III. EFFECT OF FINITE BAND GAP OF FERROELECTRIC

These difficulties originate from too strong depolarization field. However, when the electric field in insulators is too strong, the effect of the finite band gap must be examined. From this view, a Ginzburg-Landau theory [5] was presented, where the sole novelty was the rigorous formulation of ferroelectric with a finite band gap under self-consistent electric field.

This showed (1) existence of free electron e^- or free hole h^+ layer at polar discontinuities (Fig. 1) [5, 6]: ferroelectric/ insulator interface, ferroelectric free-surface, and charged domain boundaries, (2) diminished depolarization instability and size effect by screening of these carriers, and, therefore, (3) freer domain configurations. The example of (3) is the stable existence of the domains in Fig. 1(a) even without defects, and the example of (2) is the stability of P_S in Fig. 1(b).

The prediction (2) is recently named as hyper-ferroelectricity. However, in our view, this property appears in many ferroelectric, this name may not bee necessary.

IV. ELECTRON/HOLE LAYER BY POLARIZATOIN DISCONTINUITY

The experimental observations of the above prediction (1) "e^-/h^+ layer at polar discontinuities" are insufficient to verify the correctness of the theories [5-7, 36-38]. This is because these theories treated ideal ferroelectrics where the effects of defects were insignificant, whereas e^-/h^+ layer originating from defects [13-25] are prevailing owing to experimental difficulties.

Moreover, the experimental observation of electrical conduction at relatively high electric field does not mean necessarily the existence of free e^-/h^+ layer. This is because space charge limited conduction and Poole-Frenkel conduction do not need preexisting free e^-/h^+ layer. When free e^-/h^+ layer preexists throughout the current path, ohmic conductance should be observed at very low electric field. In addition, high electric field creates defects that can produce conducting region along the field [26, 27].

Considering these basics, we examine the experimental observations. Ohmic conductance at low field is absent in the reported domain boundary conduction [13-15]. This shows that little free e^-/h^+ preexists there but the barrier of injection such as band gap is lowered there. In addition, the low mobility of these domain boundaries indicates the existence of defects working as pinning. Actually, these domain boundaries are formed by high electric field along the current path, which tends to create defects there [26,27].

Therefore, the existing domain boundary conduction would be probably due to the combined effects of polar discontinuities, defect formation by high field, and carriers from the defects. For example, from a careful study Farokhipoor and Noheda concluded that the conduction of natural domain boundaries of $BiFeO_3$ thin film was due to defects [14]. Consequently, domain boundary conductions so far are not used to prove the e^-/h^+ layer by polar discontinuities at domain boundaries (Fig. 1(a)).

One of the most elaborate insulators interfaces exhibiting carrier layer, as evidenced in ohmic conduction is the $LaAlO_3/SrTiO_3$interface [1]. Because $SrTiO_3$ becomes ferroelectric by strain [39, 40], it is natural to attribute the electron layer to P_S of strained $SrTiO_3$. However, the failure of the formation of hole layers suggests the predominance of the defects such as oxygen vacancies Indeed, its growth requires high temperature (~600°C) in vacuum, where oxygen vacancies and intermixing of elements are unavoidable. This was also experimentally proved [10, 11].

Nonetheless, recent studies found the substantial contribution of P_S of $SrTiO_3$ in the electron layer formation [41-43] that has the electron mobility similar to that of Si. This mechanism is different from the original explanation of "polar catastrophe of LaO/AlO_2 layers". Therefore, the electron layer in supports partially the earlier predictions (Fig. 1(b)) [5,6]. Here, $LaAlO_3$ and $SrTiO_3$ are regarded just as a simple insulator with appropriate lattice parameters and ferroelectric induced by strain, respectively.

Free ferroelectric surface in ultrahigh vacuum (UHV) is an idealized model of insulator/ferroelectric interface, which is intrinsically well defined as immobile edge of ferroelectric.

Although $PbTiO_3$ and $BiFeO_3$ have a high P_S, they consist of volatile Pb and Bi, which evaporate even in air above 400°C and are cause of a high conductance and opaqueness of their single crystals. To avoid these sources of extrinsic conductivity, stoichiometric $BaTiO_3$ single crystals were chosen from >3000 $BaTiO_3$ crystals in Remeika lab [5]. A benefit of flux-grown $BaTiO_3$ single crystals is the atomically flat surface without polishing that causes surface damage.

Accidentally, we were able to control the P_S direction without application of electric field on the conduction path (thickness direction in Fig. 1(c)). In addition, no change of resistivity along the poling field (thickness direction in Fig. 1(c)) was found [5]. Therefore, field induced conductivity [26, 27] along the surface in Fig. 1(c) was eliminated [5].

An advantage of free surface over insulator interface is the elimination of high temperature process and high energy atoms that cause defects and intermixing. Also, the oxygen vacancy formation in UHV is suspected, but the measurement of surface resistance of $BaTiO_3$ single crystals kept in UHV at RT were unchanged over 1 year, confirming the absence of oxygen vacancies at RT. The maximum temperature T in vacuum, which was used during complete poling, was kept < 115 ~135°C depending on Curie temperature of $BaTiO_3$ crysals.

In the series of conduction measurement of the surface with $P_S\leftrightarrow$, poling T~120°C, $P_S\downarrow$, poling T~120°C, $P_S\leftrightarrow$, poling T~120°C, $P_S\downarrow$, poling T~120°C, $P_S\leftrightarrow$, poling T~120°C, $P_S\uparrow$, poling T~120°C, $P_S\leftrightarrow$, poling T~120°C, and $P_S\uparrow$ [5], where arrows $\uparrow\downarrow\rightarrow$ show the P_S directions, the conductance of the same direction was the same. That is, the conductance is determined by P_S, while it had increased with time if heating affected the conductance.

The weakness of this experiment was the absence of h^+ conduction for $P_S\downarrow$. The h^+ conduction and other properties supporting the e^-/h^+ layer by polar discontinuity were confirmed in subsequent experiments [7]. Therefore, the predictions of Fig. 1 [5] and their basis [6] are considered appropriate. In addition, single domains far wider than existing theories were formed agreeing with the prediction [6].

V. Implication of Polar-Discontinuity Carrier Layer

Section IV supports the prediction of e^-/h^+ carrier layers due to polar-discontinuity, although in many cases these layers form with aids of defects. Therefore, we examine the impacts of the e^-/h^+ carrier layers on the depolarization field in ideal ferroelectrics without defects. Figures 3(a) and 3(b) are the results for $PbTiO_3$ with an infinite band gap Eg (no e^-/h^+ carriers) and Eg = 3.2 eV, respectively [6, 31]. $PbTiO_3$ was chosen, because it has a large Free energy of ferroelectric phase and hence is resistive against depolarization-field instability.

First, critical thickness changed drastically; it is 500 nm and < 10 nm for an infinite and finite Eg, respectively, when the insulator thickness l_d is $0.77\varepsilon_d$ nm (ε_d: relative permittivity of insulator, Fig. 3). Here, the induced charge Q in Si electrode is due to P_S. Therefore, P_S is stable as far as $Q \neq 0$, irrespective of the value of Q. Secondly, in Fig. 3(b), $Q << P_S$ for $l_d > 0.25\varepsilon_d$ nm, in striking contrast with Fig. 3(a). This is because P_S is mostly screened by e^-/h^+ carrier layers inside $PbTiO_3$.

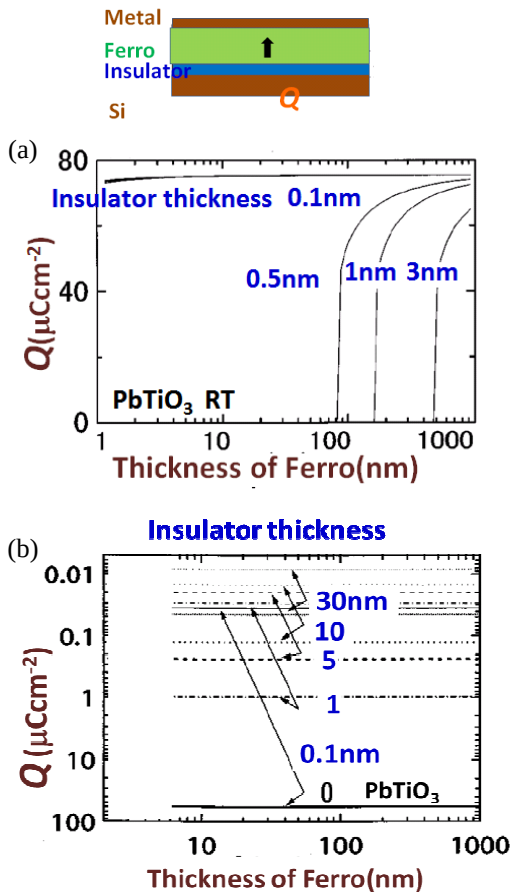

Fig. 3 The critical thickness that is the thickness for the induced charge Q = 0 and Q vs. ferroelectric ($PbTiO_3$) thickness with different SiO_2 (ε_d =3.9) for an infinite Eg (a) and a finite Eg (b) (adopted from Phys. Rev. B57, 789(1998) [5] and J. Appl. Phys. 83, 2179 (1998) [31]). p-type $PbTiO_3$ is considered. Therefore, screening is more efficient for $P_S\downarrow$ than for $P_S\uparrow$ and two lines exist for a given insulator thickness in Fig. 3(b): Q is smaller for $P_S\downarrow$ than for $P_S\uparrow$.

VI. Concluding Remarks

Ferroelectric field effect devices, which have been intensively extensively studied by many excellent researchers in industry and academics [28], are rare experiments in physics that provide quantitative properties such as induced charge for given insulator and ferroelectric thickness. Therefore, these results are not only useful for possible industrializations but also as fundamental data of ferroelectricity under depolarization field.

Thanks to these data, a theory of which predictions are consistent with many recent experiments appeared [5, 6]. It predicted (1) e^-/h^+ layer by polar discontinuity such as ferroelectric/insulator interface, ferroelectric free-surface, and charged domain boundaries, (2) diminished depolarization instability and size effects, and (3) freer domain configurations.

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REFERENCES

[1] A. Ohtomo and H. Y. Hwang, "A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface", Nature 427, pp. 423-426 (2004).

[2] J. Seidel et al., "Conduction at domain walls in oxide multiferroics" Nat Mater. 8, pp.229-234 (2009).

[3] Rojac et al., "Domain-wall conduction in ferroelectric $BiFeO_3$ controlled by accumulation of charged defects", Nat. Mat. 16, pp.322-327 (2017).

[4] Mundy et al., "Functional electronic inversion layers at ferroelectric domain walls", Nat. Mat. 16, pp.622-627 (2017).

[5] Y. Watanabe, M. Okano, and A. Masuda, "Surface conduction on insulating $BaTiO_3$ crystal suggesting an intrinsic surface electron layer", Phys. Rev. Lett. 86, pp.332-335 (2001).

[6] Y. Watanabe, "Theoretical stability of the polarization in a thin semiconducting ferroelectric", Phys. Rev. B57, pp.789-804 (1998).

[7] Review: Y. Watanabe, "Intrinsic Free Electrons/Holes at Polarization Discontinuities and their Implications for Basics of Ferroelectricity and its Origin" in H. Singh and W. Kleemann ed.,"Ferroics and Multiferroics", 57 (Trans Tech., Zurich, 2012).

[8] M. Krc̆mar and C.L. Fu, "Structural and electronic properties of $BaTiO_3$ slabs: Mechanism for surface conduction", *Phys. Rev.* B 68, 115404 (2003).

[9] Y. Watanabe,**"**$BaTiO_3$ Polar Surface in Ultrahigh Vacuum Calculated by Local Density Functional Theory with a Large Supercell", Ferroelectr. (in press).

[10] W. Siemons et al., "Origin of Charge Density at $LaAlO_3$ on $SrTiO_3$ Heterointerfaces: Possibility of Intrinsic Doping", *Phys. Rev. Lett.* 98, 196802 (2007).

[11] S. A. Pauli et al., "Evolution of the Interfacial Structure of $LaAlO_3$ on $SrTiO_3$ ", Phys. Rev. Lett. 106, 036101 (2011).

[12] A. Aird and E. K. H. Salje, J. Phys.: Condens. Matter 10, "Sheet superconductivity in twin walls: experimental evidence of WO_{3-x}"pp. L377-L380 (1998).

[13] E. K. H. Salje, Chem. Phys., "Multiferroic Domain Boundaries as Active Memory Devices: Trajectories Towards Domain Boundary Engineering" Chem.11, pp.940 (2010).

[14] S. Farokhipoor and B. Noheda, "Local conductivity and the role of vacancies around twin walls of (001)-$BiFeO_3$ thin films", J. Appl. Phys. 112, 052003 (2012).

[15] Y. Watanabe, D. Sawamura, and M. Okano, "Recurrent local resistance breakdown of an epitaxial $BaTiO_3/SrTiO_3$ heterostructure", Appl. Phys. Lett.72 (19), pp. 2415-2417(1998).

[16] Y. Watanabe, "Tunneling current through a possible all-perovskite oxide pn junction", Phys. Rev. B57, pp. R5563-R5566 (1998): References [16-18] are examplesof *p*-type conduction of $Pb(Ti,Zr)O_3$ due to PbO defects.

[17] Y. Watanabe and M. Okano, "Photodiode properties of epitaxial $Pb(Ti,Zr)O_3/SrTiO_3$ ferroelectric heterostructures", *Appl. Phys. Lett.*78, pp.1906-1908 (2001).

[18] Y. Watanab et al., "Ferroelectric/$(La,Sr)_2CuO_4$ epitaxial hetero-structure and hysteretic diode property", Physica C235-240, pp. 739-740 (1994).

[19] W. S. Baer, "Free Carrier Absorption in Reduced $SrTiO_3$", *Phys. Rev.*, 164, pp.734-738(1967).

[20] O. N. Tufte and P. W. Chapman, "Electron Mobility in Semiconducting Strontium Titanate", *Phys. Rev*. 155, pp. 796-802 (1967).

[21] C. Lee, J. Destry and J.L. Brebner, "Optical Absorption and transport in Semiconducting $SrTiO_3$", *Phys. Rev.* B 11, pp. 2299-2310(1975).

[22] J. Daniels, K.H. Härdtl, D. Hennings and R. Wernicke, "Defect Chemistry and Electrical Conductivity of Doped Barium Titanate Ceramics", *Philips Research Reports* 31, pp. 487–566 (1976).

[23] Raymond, M. V. & Smyth D. M. (1996). Defects and Charge Transport In Perovskite Ferroelectric, *J. Phys. Chem. Solids*, 57, pp.1507-1511.

[24] V.E. Henrich, G. Dresselhaus and H.J. Zeiger, "Surface Defects and the Electronic Structure of $SrTiO_3$ surfaces", Phys. Rev. B 17, pp. 4908-4921 (1978).

[25] Ch. Hagendorf, K.-M. Schindler, T. Doege and H. Neddermeyer, "An STM, XPS and LEED investigation of the $BaTiO_3$(111) surface", Surf. Sci., pp. 402-404, pp. 581-585 (1998).

[26] M. Janousch et al., "Role of Oxygen Vacancies in Cr ‐ Doped $SrTiO_3$ for Resistance ‐ Change Memory" Adv. Mater. 19, 2232 (2007).

[27] Y. Watanabe, "Review of Resistance Switching of Ferroelectrics and Oxides in Quest for Unconventional Electronic Mechanisms", Ferroelectr. 349, pp. 190–209 (2007).

[28] I.P. Batra, P. Wurfel and B.D. Silverman, "Phase-Transition, Stability, and Depolarization Field in Ferroelectric Thin-Films", Phys. Rev. B 8, pp. 3257-3265(1973).

[29] M.E. Lines and A.M. Glass, "*Principles and Applications of Ferroelectrics and Related Materials*", pp. Clarendon Press, Oxford (1977).

[30] Y. Watanabe, "Apparent Closure Domain by Standard 180^o Domain Theory and Necessity of Fundamental Screening in the Theory", Ferroelectr. 401, pp.61–64 (2010).

[31] Y. Watanabe, "Theoretical stability of the polarization in insulating-ferroelectric/semiconductor structures", J. Appl. Phys. 83, pp. 2179-2193(1998); Erratum: ibid 84, pp.3428-2193 (1998).

[32] Y. Watanabe, "Appropriate Value of Permittivity for Depolarization Field and Universal Instability of Insulating Ferroelectric Phase in Single-Domain State", *Ferroelectr.* 406, pp.35-38 (2010)..

[33] Y. Watanabe, "Proper Permittivity for Depolarization Field in Perfectly Insulating Ferroelectric and Examination of Background Permittivity", *Ferroelectr.*, 461, pp.38-43(2014).

[34] A. M. Bratkovsky and A. P. Levanyuk, "Abrupt appearance of the domain pattern and fatigue of thin ferroelectric films", Phys. Rev. Lett. 84, pp. 3177-3180 (2000).

[35] R. R. Mehta, B. D. Silverman, and J. T. Jacobs, "Depolarization fields in thin ferroelectric films", *J. Appl. Phys*. 44, 3379 (1973).

[36] Y. Watanabe and D. Sawamura, "Thermodynamic Stability of the Spontaneous Polarization and the Space Charge layer in Ferroelectric/Semiconductor Heterostructures", *Jpn. J. Appl. Phys.* 36, pp. 6162-6166 (1997).

[37] Y. Watanabe et al., "Bipolar Carrier (e^-/h^+) Layer on Clean Surface of Insulating $BaTiO_3$ Crystal Intrinsic to Ferroelectrics, *Ferroelectrics*, 367, pp. 23-37 (2008)

[38] Y. Watanabe, "Microscopic derivation of free energy under electric field in ferroelectric and ferroelectric heterostructures containing free carriers", *Ferroelectrics* 333, pp.57-67 (2006).

[39] H. Uwe and T. Sakudo, "Stress-induced ferroelectricity and soft phonon modes in Sr TiO_3", *Phys. Rev*. B 13, pp.271-286 (1976).

[40] W.J. Burke and R.J. Pressley, "Stress induced ferroelectricity in $SrTiO_3$" *Solid State Commun*. 9, pp.191-195 (1971).

[41] T. Gunter et al., "Spatial inhomogeneities at the $LaAlO_3/SrTiO_3$ interface: Evidence from second harmonic generation", Phys. Rev. B 86, 235418 (2012).

[42] A. Savoia et al.," Polar catastrophe and electronic reconstructions at the $LaAlO_3/SrTiO_3$ interface: Evidence from optical second harmonic generation" Phys. Rev. B 80, 075110 (2009).

[43] B. Kalisky et al., "Locally enhanced conductivity due to the tetragonal domain structure in $LaAlO_3/SrTiO_3$ heterointerfaces", Nat. Mat. 12, 1091 (2013).