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Ferroelectricity at the nanoscale

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Abstract

The properties of ferroelectrics at the nanoscale are reviewed. The term nanoscale is here related to the ferroelectric film thickness (which is by an order of magnitude the size of the critical domain nucleus). The three aspects considered are ferroelectric switching, the scaling of the coercive field, and the bulk photovoltaic effect. While ferroelectricity at the nanoscale has a twenty-year history of study, it is only in the last few years that perovskite ferroelectric films have become a focus of interest.

1. Introduction: Some Historical Remarks

In 1945–1946, Vul [1] in Russia and von Hippel [2] in the US discovered ferroelectric properties in BaTiO₃, a discovery that stimulated Ginzburg to develop the ferroelectric mean-field theory (also known as the Landau-Ginzburg-Devonshire, or LGD, theory) [3, 4].

The LGD theory predicts switching to occur for $E > E_c$, where E_c is the coercive field. We use the term ‘intrinsic coercive field’ to refer to the value of E_c determined from the LGD theory; hence, the term intrinsic (or uniform) for LGD switching. Figure 1, taken from Ginzburg’s work [3], shows the LGD-calculated dependence of the free energy ϕ on the polarization P for different values of the external field E and illustrates intrinsic (uniform) switching. It can be seen that LGD switching has a characteristic limit field, $E = E_{c,in}$, below which no switching occurs. Until 1998, no one ever observed intrinsic switching, either in bulk crystals or in films. The measured coercive field $E_{c,ex}$ was found to be 2–3 orders of magnitude less than the intrinsic values $E_{c,ex} \ll E_c$ in predicted by the LGD theory.

This discrepancy remained unresolved for some years until the discovery of domains in Seignette’s salt by Chernyshova and coworkers [5]. Later, Merz discovered that BaTiO₃ has a

domain structure and that polarization switching is due to the motion of domains in an external field [6]. Indenbom reached the same conclusion from his study of Seignette’s salt [7]. Then Ishibashi and Takagi [8] used Kolmogorov’s statistics to develop a theory of domain (extrinsic) switching, known as the Kolmogorov-Avrami-Ishibashi (KAI) theory. A comprehensive review of the intrinsic (domain) mechanism is given in Reference [9].

Thus, while the LGD mean-field theory is successful in explaining the totality of ferroelectric phenomena, including first-order close to second-order ferroelectric transitions,

Figure 1. Switching in the LGD theory.

it so far has failed to account for the switching phenomenon and its details. The discovery and study of Langmuir-Blodgett (LB) polymer ferroelectric nanofilms [10, 11] changed this situation. The LB method allows controlling the film thickness to a single monolayer (0.5 nm) and uses ellipsometry and atomic force microscopy to control the species and orientation of molecules.

The properties and growth of LB nanofilms of polyvinylidene fluoride-trifluoroethylene copolymer have been studied by a number of authors [12–15]. While the study and application of thin ferroelectric films has a long history [16], it is the LB method that first enabled the fabrication and study of films with a thickness of the order of the critical domain nucleation size. Because, as is known, critical domain nuclei have their size l^* in the range ≈ 1 –10 nm [16–18], nanosize ferroelectric films allow only nucleation and initial domain growth. In spite of this, ferroelectric LB films exhibit the phenomenon of switching [11], something that the KAI theory does not explain.

2. Switching at the nanoscale

It was conjectured in [19, 20] that switching in ferroelectric films in the nanorange (1–10 nm) occurs by an intrinsic (uniform) LGD mechanism. The kinetics of intrinsic switching are described within the uniform mean-field framework by the Landau-Khalatnikov equation

$$\xi \frac{dP}{dt} = -\alpha P - \beta P^3 - \gamma P^5 + E \quad (1)$$

where P is the spontaneous polarization, α , β , and γ are the well-known Landau-Ginzburg coefficients for first-order ferroelectrics, E is the external field, and ξ is the damping coefficient. Equation (1) admits the critical solution [19]

$$\tau^{-1} \simeq \frac{1}{\tau_0} \left(\frac{E}{E_{c,in}} - 1 \right)^{1/2} \quad (2)$$

where τ is the switching time, $\tau_0 \approx 6.3\gamma\xi/\beta^2$, $E_{c,in}$ is the intrinsic coercive field, and $E_{c,in} \approx P/\epsilon\epsilon_0$. As can be seen from Equation (2), switching occurs only for $E > E_{c,in}$ and does not occur for $E < E_{c,in}$.

Thus, as already noted, intrinsic LGD switching is characterized by a limit field $E = E_{c,in}$ in contrast to the KAI domain mechanism, where this notion is irrelevant. In the simplest case, the KAI theory yields the following expression for the switching time [8]:

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{E_0}{E}\right) \quad (3)$$

where τ_0 and E_0 are constants.

3. Kinetics of intrinsic switching

Intrinsic LGD switching was first discovered in a 1 nm thick LB copolymer film [11], and its kinetics were extensively studied using Merz's and Chynoweth's methods [19, 21, 22] and piezoelectric atomic force microscopy (PAM) [23, 24].

In Figure 2, the inverse switching time (Figure 2b) measured by the Merz method (Figure 2a) is shown as a function of the external voltage V for an LB polymer. In Figure 2b, the value $E_{c,in} \approx 10^9$ Vcm $^{-1}$, corresponding to the thickness $l = 15$ nm, correlates with the value of the intrinsic coercive field for

polyvinylidene fluoride-trifluoroethylene [20]. The continuous curve in Figure 2b corresponds to expression (2). Figure 2c shows the same plots for the thicknesses $l = 5, 15$ and

Figure 2. Intrinsic and extrinsic switching in a ferroelectric copolymer. t_m indicates the maximum of the switching curve. ML stands for monolayer.

Figure 3. (a) Epitaxial BTO film. Electron diffraction images of (b) MgO/Pt and (c) Pt/BTO interfaces.

50 nm (10, 30, and 200 monolayers, respectively). The thicker films exhibit the behavior predicted by the KAI theory in Equation (3). Two films with thicknesses of 5 nm and 15 nm (10 and 30 monolayers), despite experimental scatter, show a limit value $V = 4$ V. The continuous curves correspond to Equation (2) for 5 nm and 15 nm and to Equation (3) for 50 nm (100 monolayers). The data were obtained using the Chynoweth method. PAM measurements yielded the same results [23, 24].

The observation of uniform LGD switching in ferroelectric polymer films [19, 21, 24] in the nanoscale range led many to conclude that this switching behavior is a polymer-specific exception [9]. Perovskite ferroelectric films in the nanometer range were obtained fairly recently and have not yet been investigated for switching uniformity. A comprehensive review on the growth of perovskite superlattices in the nanoscale range is given in Reference [25]. Ferroelectricity was found in perovskite films with a thickness of three unit cells (1.2 nm) [26–29], but no study has been made on whether they exhibited switching is intrinsic. The idea of uniform switching in PbTiO_3 nanofilms was suggested in only one work, study [30], which failed to study switching kinetics, however.

Uniform intrinsic switching in perovskites was first discovered in Reference [31], which used a capacitor circuit and atomic force microscopy to study switching kinetics in ultrathin heteroepitaxial BaTiO_3 films and which demonstrated good agreement between the observed limit coercive field and its LGD value.

In References [32, 33], ultrathin barium titanate (BTO) films were laser epitaxially grown on a Pt/MgO (100) substrate in a single vacuum cycle, and the resulting composite systems were studied for their structural properties (including the film thickness) using Rutherford backward scattering spectroscopy and transmission electron microscopy. The heteroepitaxial growth of BR films on a Pt surface is illustrated by the data obtained on the MgO/Pt and Pt/ BaTiO_3 interfaces using high-resolution Fourier-transform electron microscopy (Figure 3). The thickness of the BaTiO_3 films, $l = 2, 8$, and 40 nm, was measured (to within a 10-percent or better accuracy) by Rutherford backward scattering from 2 MeV He^{++} ions [32]. To perform capacitor measurements, a second (Au) electrode was deposited on a barium titanate film in an ultra-high vacuum

Figure 4. Measurements on a capacitor using PAM.

Figure 5. Intrinsic and extrinsic switching in a nanometer BTO film.

(Figure 4). The measurements were made with a piezoelectric atomic force microscope with its tip in contact with the gold electrode. The top 20 nm gold electrode was deposited on the barium titanate surface in an ultra-high vacuum (see Figure 4).

All films in the thickness range 4–40 nm exhibited a stable monodomain state.

The difference between intrinsic behavior and extrinsic behavior is shown in Figure 5, which plots the switching rate versus the applied voltage for an ultrathin (8 nm) epitaxial barium titanate film (Figs 5a, b) and for a 1mm thick single-crystal [001] plate of barium titanate (Figure 5c). Shown in Figure 5a is a τ^{-2} versus V plot for barium titanate in a capacitor. Figure 5b is the same for the tip in contact with the free surface of the film (the so-called tip regime). The experimental

Figure 6. (a) Schematic of domain switching and (b) schematic of uniform switching (from Reference [36]).

data are in good agreement with Equation (1) and indicate the coercive field $E_c = E_{c,in}$. Despite the small difference in the switching time, both regimes exhibit the same intrinsic switching behavior.

Referring to Figure 5c, we see that for a single crystal, on the contrary, the switching kinetics are in agreement with Equation (3), with switching occurring at $V = V_{c,ex} \ll V_{c,in}$.

Switching kinetics measurements confirm the occurrence of homogeneous switching in nanoscale ferroelectric films with a thickness of the order of the critical domain nucleation size. If we change from crystals to ferroelectric films, the KAI mechanism is superseded by the uniform LGD mechanism. In this thickness range, there is competition between these two mechanisms, both of which depend on the film thickness and the external field. This point has recently been given a first-principle justification [34]. Transitions between the two mechanisms are due to the difference in the switching time versus field dependence between thick films (Equation (3), an exponential dependence) and thin films (Equation (2), a slower dependence). The occurrence of extrinsic switching at high fields was recently discovered in Reference [35]. We believe that this competition between the two mechanisms is a common feature of all ferroelectric films comparable in thickness to the size of the critical domain nucleus.

Clearly, the phenomenological LGD theory cannot explain how switching works microscopically. Some preliminary notes on this point have already appeared [30]. In accordance with Reference [30], we suggest the following microscopic mechanism of switching (Figure 6).

In the nanoscale range, both the LGD and KAI switching mechanisms operate simultaneously. At thicknesses close to the critical domain nucleation size (which is in the range 1–10 nm according to References [16–18]; Miller and Weinreich speak of 5 nm), the dominant mechanism is the inherent uniform one, implying domainless switching in such nanoscale films.

4. Coercive field scaling

All ferroelectric films have their coercive field dependent on the thickness, $E_{c,ex} = E_{c,ex}(l)$. The intrinsic LGD coercive field $E_{c,in}$ is thickness independent and determined by the Landau-Ginzburg coefficients [20].

Figure 7a plots $E_c = E_c(l)$ for an LB film of ferroelectric copolymer P[VDF-TrFE] [20]. It is seen that for the film thickness less than 10 nm, $E_c = E_{c,in} \approx 10^9 \text{ V m}^{-1}$, and the coercive field is independent of the film thickness. The coercive field strength is in good agreement with the intrinsic LGD value. Thicker films, which were prepared by the spinning technique, exhibit

Figure 7. (a) Scaling of the coercive field in a ferroelectric copolymer. (b) Inverse capacitance of the capacitor as a function of the film thickness.

scaling behavior. The authors of Reference [20] therefore conjectured that 1–10 nm copolymer films exhibit uniform switching, as in Equations (1) and (2), as indeed was later found in [19, 21–24]. In contrast to this, in films thicker than 10 nm, the coercive field is found to be thickness dependent, implying the domain switching dynamics [8].

The results shown in Figure 7a were obtained in an Al-P[VDF-TrFE]-Al capacitor using the Sawyer-Tower method.

It was hypothesized in [36] that the saturation in Figure 7a is due to the Thomas-Fermi screening gap between the electrode and the copolymer film. However, no dependence of the inverse capacity of the capacitor on the film thickness was observed (Figure 7b) [37].

Here, for the first time, a scaling behavior of the same type is reported for nanoscale barium titanate films grown by laser epitaxy [38]. Measurements were performed on a Pt-BaTiO₃-Au capacitor using PAM (see Figure 4). Electrodes were formed on a barium titanate surface by lithography and were circular with a radius of a few micrometers. Figure 8 shows hysteresis loops obtained for films with thicknesses of 3, 8, and 40 nm (Figs 8a–c). Also shown is the variation of the coercive field with the film thickness in the range 3–40 nm (Figure 8d). Scaling occurs at thicknesses above 10 nm. In the range 3–10 nm, the coercive field is only weakly thickness dependent, and its magnitude $E_{c,in} \approx 10^8 \text{ V m}^{-1}$ is in close agreement with that given by the LGD theory. Accordingly, films with thicknesses of 3 and 8 nm exhibit uniform LGD switching, as given by Equations (1) and (2), whereas thicker films follow the domain dynamics, as in Equation (3).

Figure 8. Hysteresis in a BTO film with the thickness (a) 3nm, (b) 8 nm, and (c) 40 nm; and (d) coercive field scaling.

5. Bulk photovoltaic effect in nanoferroelectrics

In this section, we make some brief preliminary remarks on the bulk photovoltaic effect (BPE) in the nanometer range.

Until the 1970s, there were two known varieties of the photovoltaic effect. The reasons for the first of these, the Dember effect, are the nonuniform illumination of the crystal and the strong absorption of light; the effect is then due to the diffusion of nonequilibrium carriers and the mobility difference between holes and electrons. The second variety is due to the separation of nonequilibrium carriers at crystal nonhomogeneities, the well-known example being the photovoltaic effect on p-n junctions currently used in solar cells. Thus, the photovoltaic effect as known until the early 1970s was due to either inhomogeneities in or nonuniform illumination of the crystal. In either case, the photovoltage generated in the crystal (or in an individual p-n junction) does not exceed the band gap width of the crystal (which is a few volts).

In the early 1970s, another effect, the so-called bulk photovoltaic effect, was discovered [39], which arises when a crystal without central symmetry is exposed to uniform illumination. Unlike its earlier counterparts, neither crystal nor illumination inhomogeneities play any role in this effect. There are two major points about the BPE: the bulk photovoltaic current depends on the light polarization, and the photovoltage in an open circuit crystal can exceed the band gap by orders of magnitude. The BPE is observed only in noncentrosymmetric crystals, and hence for in only twenty pyroelectric point symmetry

groups. In other words, we here have an analogy to the violation of parity in weak interactions, for example, in neutron beta decay in ^{60}Co experiments (which brought the Nobel Prize in physics to Lee and Yang in 1957 [40, 41]). Landau was the first to hypothesize (in his lecture at the Shubnikov Institute of Crystallography in 1957) that the nonconservation of parity has a relation to the asymmetry of the Universe.

The microscopic BPE theory introduces a violation of the detailed balance principle for photoexcited carriers in noncentrosymmetric crystals [39]. The detailed balance principle assumes that the probability $W_{kk'}$ of transition from the state with a momentum k' to the state with a momentum k equals that of the opposite transition, $W_{k'k}$. Earlier, it was believed that this principle holds in kinetic theory for all solids, but already Boltzmann questioned this. In centrosymmetric crystals (such as Ge or Si), this principle does apply, and the BPE, accordingly, does not exist. In noncentrosymmetric crystals, where $W_{kk'} \neq W_{k'k}$, the violation of detailed balance leads to a nonequilibrium momentum distribution of conduction-band electrons or holes, producing a photovoltaic current in a homogeneous crystal under uniform illumination. This is schematically illustrated in Figure 9.

Irrespective of the microscopic mechanism, the BPE involves the excitation of nonthermalized electrons (holes) in the crystal. From Figure 9a, which illustrates the intrinsic excitation of a centrosymmetric crystal, we see that the electron distribution in the band is symmetric and that the current is absent. The excitation of a noncentrosymmetric crystal

Figure 9. (a) Symmetric distribution of nonequilibrium carriers in a band of a centrosymmetric crystal; (b) nonsymmetric distribution of non-equilibrium carriers in a crystal with no center of symmetry.

(Figure 9b) results in the nonthermalized carriers having their momenta distributed asymmetrically (as shown by the arrow). The photoexcited nonthermalized carriers lose their energy and fall to the bottom of the conduction band, which causes them to shift by l_0 and gives rise to the bulk photovoltaic current

$$J = \alpha G^L I,$$

where α is the absorption coefficient and I is the light intensity. The amplitude of the third-rank tensor G^L is

$$G^L = e l_0 \zeta \varphi (h\nu)^{-1} \quad (4)$$

where φ is the quantum yield, the parameter ζ characterizes the excitation asymmetry and depends on the detailed balance violation mechanism, e is the electron charge, and G^L is a component of the third-rank tensor, whose experimental value is 10^{-8} – 10^{-9} cm V $^{-1}$. In accordance with Reference [39], $\zeta \approx 10^{-1}$ – 10^{-2} , and l_0 is in the range 10–100 nm. If the shift of a nonthermalized electron is of the order of the ferroelectric film thickness, the energy conversion efficiency η can be large. The estimate in [39] is

$$\eta = \frac{1}{4} G^L l_0 \zeta (\mu\tau)^{-1} \quad (5)$$

where in the nanometer range (10–100 nm), the mobility μ and the lifetime τ are nonthermalized.

Substituting $l_0 = 10$ – 100 nm, $G \approx 10^{-8}$, and $\zeta \approx 10^{-1}$ – 10^{-2} in Equation (5) for barium titanate films, we obtain

$$\eta \approx 10^{-15} (\mu\tau)^{-1} \quad (6)$$

The thermalization time is $\tau \approx 10^{-12}$ – 10^{-14} s [39]. However, the uncertainty in the estimate of the effective mass of the polaron prevents estimating the mobility of a nonthermalized electron μ .

Finally, we mention a series of recent experiments [42–44] that measured the photovoltaic effect and the energy conversion efficiency in the nanometer range, but failed to uncover the physical mechanism of these phenomena.

6. Conclusion

To conclude, ferroelectric properties in the nanometer range occur not because of any dimensional effect but because of the coexistence of intrinsic and extrinsic switching mechanisms, their respective roles depending on the film thickness and the external field. For ferroelectric films with thickness $l > l^*$, the dominant factors are the extrinsic coercive field and switching. For $l < l^*$, intrinsic uniform switching and the coercive field take over, as they should according to the LGD phenomenology.

The LGD mean-field theory of 1945 was developed for a homogeneous medium and was unable to explain the details of switching. The 1970 KAI theory developed for a domain-structured medium both explained the switching kinetics and predicted the value of the coercive field in crystals and films. Ultrathin films with a thickness of the order of the critical domain nucleation size can be considered homogeneous. For such films, the LGD phenomenology accounts for all ferroelectric properties, including switching (see the literature from 1993 to 2013).

The bulk photovoltaic effect in the nanometer range seems to hold promise for high-efficiency energy conversion.

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References

1. Vul B M, Gol'dman I M *Dokl. Akad. Nauk SSSR* **46** 154 (1945)
2. von Hippel A et al. *Ind. Eng. Chem.* **38** 1097 (1946)
3. Ginzburg V J. *Phys. USSR* **10** 107 (1946); *Zh. Eksp. Teor. Fiz.* **15** 739 (1946)
4. Ginzburg V L *Usp. Fiz. Nauk* **38** 490 (1949)
5. Klassen-Neklyudova M V, Chernyshova M A, Shternberg A A *Dokl. Akad. Nauk SSSR* **63** 527 (1948)
6. Merz W J *Phys. Rev.* **95** 690 (1954)
7. Indenbom V L, Chernyshova M A *Izv. Akad. Nauk SSSR Ser. Fiz.* **22** 1469 (1958)
8. Ishibashi Y, Takagi Y J. *Phys. Soc. Jpn.* **31** 506 (1971)
9. Tagantsev A K, Cross L E, Fousek J *Domains in Ferroic Crystals and Thin Films* (New York: Springer, 2010)
10. Palto S et al. *Ferroelectrics Lett.* **19** 65 (1995)
11. Bune A V et al. *Nature* **391** 874 (1998)
12. Blinov L M et al. *Phys. Usp.* **43** 243 (2000); *Usp. Fiz. Nauk* **170** 247 (2000)
13. Fridkin V M *Phys. Usp.* **49** 193 (2006); *Usp. Fiz. Nauk* **176** 203 (2006)
14. Fridkin V M, Gaynutdinov R V, Ducharme S *Phys. Usp.* **53** 199 (2010); *Usp. Fiz. Nauk* **180** 209 (2010)
15. Ducharme S, Palto S, Fridkin V, in *Handbook of Thin Film Materials* Vol. 3 (Ed. H S Nalwa) (San Diego: Academic Press, 2002)
16. Scott J F *Ferroelectric Memories* (Berlin: Springer, 2000)

17. Shin Y-H et al. *Nature* **449** 881 (2007)
18. Chernov A A *Sov. Phys. Usp.* **4** 116 (1961); *Usp. Fiz. Nauk* **73** 277 (1961)
19. Vizdrik G, Ducharme S, Fridkin V M, Yudin S G *Phys. Rev. B* **68** 094113 (2003)
20. Ducharme S et al. *Phys. Rev. Lett.* **84** 175 (2000)
21. Geivandov A R et al. *JETP* **99** 83 (2004); *Zh. Eksp. Teor. Fiz.* **126** 99 (2004)
22. Ievlev A, Verkhovskaya K, Fridkin V *Ferroelectrics Lett.* **33** 147 (2006)
23. Gaynutdinov R V et al. *Appl. Phys. Lett.* **99** 142904 (2011)
24. Gaynutdinov R et al. *J. Phys. Condens. Matter* **24** 015902 (2012)
25. Rabe K M, Ahn C H, Triscone J-M (Eds) *Physics of Ferroelectrics. A Modern Perspective* (Berlin: Springer, 2007)
26. Fong D D et al. *Science* **304** 1650 (2004)
27. Tybell T, Ahn C H, Triscone J-M *Appl. Phys. Lett.* **75** 856 (1999)
28. Lichtensteiger C et al. *Phys. Rev. Lett.* **94** 047603 (2005)
29. Pertsev N A et al. *Appl. Phys. Lett.* **83** 3356 (2003)
30. Highland MJ et al. *Phys. Rev. Lett.* **105** 167601 (2010)
31. Gaynutdinov R et al. *Physica B* **424** 8 (2013)
32. Zenkevich A et al. *Appl. Phys. Lett.* **99** 182905 (2011)
33. Zenkevich A et al. *Thin Solid Films* **520** 4586 (2012)
34. McCash K, Srikanth A, Ponomareva I *Phys. Rev. B* **86** 214108 (2012)
35. Chanthbouala A et al. *Nature Mater.* **11** 860 (2012)
36. Chandra P et al. *Ferroelectrics* **313** 7 (2004)
37. Bai M et al. *J. Appl. Phys.* **95** 3372 (2004)
38. Gaynutdinov R et al. *JETP Lett.* **98** 339 (2013); *Pis'ma Zh. Eksp. Teor. Fiz.* **98** 380 (2013)
39. Sturman B I, Fridkin V M *The Photovoltaic and Photorefractive Effects in Noncentrosymmetric Materials* (Philadelphia: Gordon and Breach Sci. Publ., 1992)
40. Yang C *Usp. Fiz. Nauk* **66** 79 (1958)
41. Lee T *Usp. Fiz. Nauk* **66** 89 (1958)
42. Ji W, Yao K, Liang Y C *Adv. Mater.* **22** 1763 (2010)
43. Qin M, Yao K, Liang Y C *Appl. Phys. Lett.* **93** 122904 (2008)
44. Ichiki M et al. *Appl. Phys. Lett.* **84** 395 (2004)