

Transition-state-theory-based interpretation of Landau double well potential for ferroelectrics

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Abstract—Existence of quasi-static negative capacitance (QSNC) was proposed from an interpretation of the widely accepted Landau model of ferroelectrics. However, many works showed not to support the QSNC theory, making it controversial. In this letter we show the Landau model when used together with transition-state-theory, can connect various models including first-principles, Landau, Preisach and nucleation limited switching while it does not predict the existence of QSNC.

Index Terms—Landau model, Quasi-static Negative capacitance.

I. INTRODUCTION

STEPP-subthreshold-slope in the transfer characteristics of MOSFETs is needed to keep on scaling the supply voltage (V_{DD}) that would in turn reduce power dissipation without sacrificing performance. In 2008 [1] it was proposed from an extended interpretation of the Landau model that QSNC exists in ferroelectric (FE) materials that can provide the required steep slope operation of MOSFETs. Many mathematical models are available for describing ferroelectricity. Physics-based first principles models like DFT gives clear insight to the working of FE at a large computational cost. On the other hand, the least expensive phenomenological models (e.g., Preisach, KAI, NLS [2]) do not pay serious attention to the underlying physics. Landau model was originally designed for describing phase transition phenomena using a double well thermodynamic potential. Minimization of that potential gives an S-shaped polarization-field relation, largely referred to as the “S-curve”. QSNC theory states a FE is stabilizable on the negative slope region of the S-curve by applying a charge boundary condition (CBC) by stacking the FE with a dielectric (DE) and/or with a semiconductor channel of a MOSFET [1]. The QSNC theory was not universally accepted by the scientific community. Experimental works that claimed to capture any signature of QSNC [3] or the S-curve [4] have been shown to be a misinterpretation of measurement data, independently by D. A. Antoniadis from MIT [5], T. P. Ma from Yale [6], J. A. Kittl from Samsung [7] and many others. We also showed the same by direct application of CBC [8]. It is yet to be shown whether prediction of the QSNC is intrinsic to the Landau model or not. In this article we show that the double well potential comes from the physics-based model. A phenomenological adjustment translates it to the Landau model with a better quantitative predictability. Finally, we describe the polarization switching dynamics using transition state theory taking the Landau potential as two-state system. Such a model bridges all the model types, correctly predicts experimental outcomes and does not predict the existence of QSNC. We keep the discussion particularly for HfO_2 based

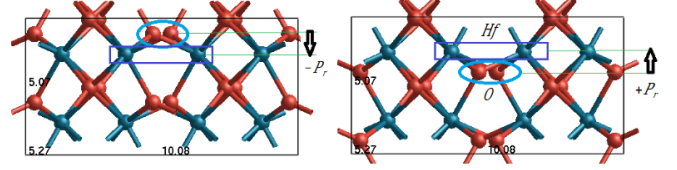


Fig. 1. Two possible minimum energy atomic configurations of orthorhombic HfO_2 with up and down polarization.

ferroelectric as it is technologically most relevant, however the outcome of the work is general for any FE system.

II. ATOMISTIC MODEL TO LANDAU MODEL

Two minimum energy configurations of orthorhombic HfO_2 is shown in Fig. 1, Orthrhombic HfO_2 has two possible minimum energy atomic configuration, where the displacement between Hf and O atoms in each of them give rise to polarization $\pm P$. Switching between $+P$ and $-P$ or vice-versa involves transformation between two structures [9]. We calculate the minimum energy path needed for the process to occur using a Nudged Elastic Band (NEB) approach with the climbing image algorithm [10]. During switching, energy and P of images (snapshots of the atomic positions during switching) are computed by density functional theory (DFT) with a $2 \times 2 \times 2$ Monkhorst–Pack k-point mesh using mixed (Gaussian and plane wave) basis within local density approximation (LDA) and Berry phase approach, respectively.

Fig. 2a shows multiple branches of continuously varying P_m (P of m^{th} image). It is attributed to the uncertainty in P computation caused by crystal’s periodicity, given by [11]

$$P_m = P_m + nQ_n \quad (1)$$

where Q_n is “quantum of polarization”, and n is an integer. Image-1 and 29 must give remnant polarization, $-P_r$ and $+P_r$ respectively, as they correspond to the two minimum energy atomic configurations (Fig. 1). Therefore, the symmetric branch in Fig. 2a gives P .

Fig. 2b shows computed energy (at temperature $T=0K$) as a function of P . Results obtained from NEB is fitted with Landau model (Fig. 2b) that gives the energy as a function of P as-

$$U = \alpha P^2 + \beta P^4 - EP \quad (2)$$

Here E is applied electric field, α and β are Landau parameters. Minimization of U with respect to P gives $P-E$ relationship at steady-state as shown in Fig. 2c, also referred to as “S-curve”. The broken line, that has a negative slope and therefore QSNC, represents the maximum in the middle of the

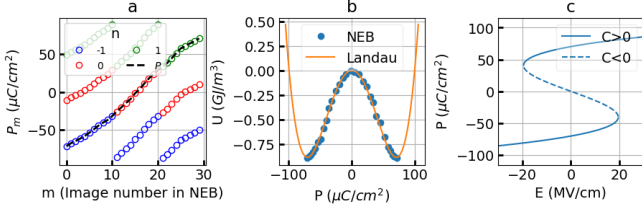


Fig. 2. a) Polarization in the m^{th} image of the NEB simulation, given by equation 1. Different parallel branches are created due to the uncertainty imposed by the quantum of polarization, b) Energy profile as a function of P (from Fig. 2a) fitted with Landau model, c) Minimization of the Landau potential gives the S-curve

Landau potential where the curvature of the profile is negative (Fig. 2b).

III. PHENOMENOLOGICAL/STATISTICAL MODEL

Small regions of ferroelectric can switch their P independent of each others, called hysteron. Their statistical behavior is described by phenomenological models. We showed Preisach (a steady-state model) and NLS (transient model) can describe P switching of HfO_2 at a low computational cost [2]. According to NLS model the switching time constant τ of j^{th} hysteron is given by Merz law as-

$$\tau_j = \tau_0 \exp\left(\frac{E_a}{E}\right)^\alpha \quad (3)$$

where E_a and E are the activation field and the applied electric field, respectively, and τ_0 is the characteristic nucleation time and α is a phenomenological constant. The time dependent polarization is then given by-

$$P(t) = 1 - \left\langle \exp\left\{-\left(\frac{t}{\tau_j}\right)^\alpha\right\}\right\rangle \quad (4)$$

In the following section we show such phenomenological models come out from the double-well potential when used together with transition-state theory. In addition, that does neither predict the S-curve nor QSNC.

IV. TRANSITION-STATE-THEORY

The minima of the Landau potential profile (Fig. 2b) lead to the minimum-energy atomic arrangements. Therefore, the minima denote a thermodynamic state where a hysteron can be found. All the hysteron in a FE get distributed in the two states. Application of external electric field tilts the energy profile and thereby changes the barrier height between the states as shown in Fig. 3a. From here the transition state theory starts with the following postulates-

- Switching between the states is an Arrhenius process.
- Barriers W_1 and W_2 are “kinetic barriers” for switching.

Let us call the two states as state-1 and state-2 respectively. If all the hysteron were poled to state-1 or state-2 then the net polarization of the system would be $-P_r$ or $+P_r$ respectively. Merz law (eq. 3) has been shown to be equivalent to the Arrhenius process of crossing a barrier (i.e., transition-state-theory) [12].

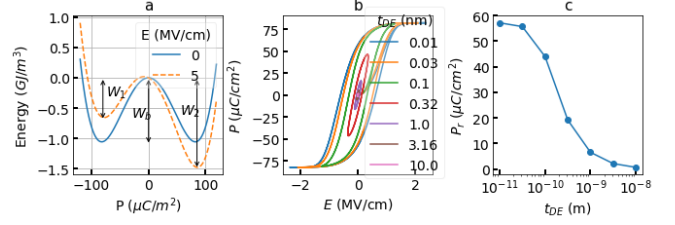


Fig. 3. a) Double well energy profile under applied electric field. Solution of master equation in FE-DE stack gives b) $P-E$ behavior of FE, c) P_r as a function of dielectric thickness

$W_{1,2}$ as a function of applied electric field is given by-

$$\begin{aligned} W_1 &= V(W_b - mqE/A) \\ W_2 &= V(W_b + mqE/A) \end{aligned} \quad (5)$$

Here A and V denotes the area and volume of the hysteron respectively, W_b is the barrier height at zero field, q is the elementary charge, m is a number giving the amount of polarization charge (in the unit of q) that a hysteron contains. The time evolution of the occupation probability of states in a multi-state system is given by Pauli's master equation [13] as-

$$\begin{aligned} \frac{dp_1}{dt} &= a_{1 \leftarrow 2} p_1 - a_{2 \leftarrow 1} p_2; \quad a_{1 \leftarrow 2} = \nu_0 \exp\left(\frac{-W_2}{kT}\right) \\ \frac{dp_1}{dt} &= -a_{1 \leftarrow 2} p_1 + a_{2 \leftarrow 1} p_2; \quad a_{2 \leftarrow 1} = \nu_0 \exp\left(\frac{-W_1}{kT}\right) \end{aligned} \quad (6)$$

Here $a_{l \leftarrow m}$ is the transition rate from state m to l , ν_0 is escape frequency, k is the Boltzmann constant and T is the temperature. From the solution of eq. 6, total polarization of the FE is obtained as-

$$P = -P_r p_1 + P_r p_2 \quad (7)$$

At a constant electric field an analytical solution of the eq. 6 is obtained as-

$$\begin{aligned} p_1(t) &= p_1(0)e^{(-\frac{t}{\tau})} + p_1(\infty)\left(1 - e^{(-\frac{t}{\tau})}\right) \\ p_2(t) &= 1 - p_1(t) \end{aligned} \quad (8)$$

Here $p_i(0)$ and $p_i(\infty)$ are the fractional occupation of state- i at $t = 0$ (initial) and $t = \infty$ (at steady-state) respectively, and $\tau = (a_{1 \leftarrow 2} + a_{2 \leftarrow 1})^{-1}$ is a time constant for switching. The Preisach model assigns a distribution of the coercive field to $p_1(\infty)$ and $p_2(\infty)$ for many hysteron. The remaining term in eq. 8 is $\left(1 - e^{(-\frac{t}{\tau})}\right)$. Comparing it against eq. 4 it is seen that the NLS model uses the very same equation with an assumption that τ is distributed over an exponentially broad spectrum. Overall response of the system is obtained by summing-up the contribution of all the τ values. In other words, equation 8 encompasses both the Preisach and the NLS models within itself, provided that statistical distributions are introduced. This way it can bridge the physics-based NEB model with the statistical models (that have accurate predictability of experimental results) while automatically absorbing Landau double-well potential in it. Next critical question to answer is, whether such interpretation predicts the existence of QSNC under CBC in a FE-DE stack.

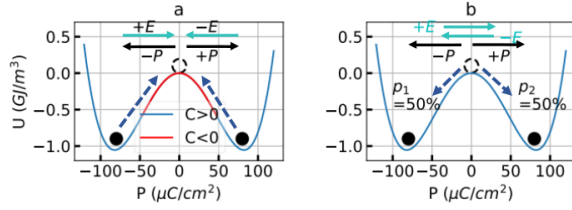


Fig. 4. Difference in the interpretation of zero net-polarization state of ferroelectric-dielectric stack caused by the depolarization field E (eq. 9)- a) according to QSN theory, E pushes FE from the minima to the TOB b) according to transition-state theory, E equally distributes the hysteron in both wells.

V. FERROELECTRIC-DIELECTRIC STACK

The electric field experienced by the FE in a FE-DE stack is given by

$$E = \frac{\epsilon_0 \epsilon_{DE}}{t_{DE}} \frac{V_{stack} - P}{\epsilon_{FE} + \epsilon_{DE} \frac{t_{FE}}{t_{DE}}} \quad (9)$$

Here, V_{stack} is the voltage applied across the ferroelectric-dielectric stack, P is the polarization given by equation 6 and 7, t_{FE}, t_{DE} and $\epsilon_{FE}, \epsilon_{DE}$ are thicknesses and relative permittivity of FE and DE layers respectively. Therefore, equations 5, 6, 7 and 9 are coupled. We solve the coupled equation for sinusoidal V_{stack} . Fig. 3b shows the P as a function of field in the FE for $t_{FE} = 20nm$ and various values of t_{DE} . Note the behavior obtained this way (Fig. 3b) is always hysteretic and does not show an S-curve (Fig. 2c). Consequently, it does not predict the existence of QSN. It is because in the Master equation approach, only the minimum in the potential profile represents a physical state where a hysteron can be found. The polarization at zero electric field, is extracted from Fig. 3b and plotted in Fig. 3c. When the thickness of the DE increases the polarization decreases with it. It is because thicker dielectric increases the depolarization field that suppresses the polarization. Note that this is the simplest case with an ideal FE-DE interface. In reality, strain boundary condition, interface quality etc. will also play a role in determining the polarization state. The trend has a good qualitative agreement with experimental results reported in [12]. When the dielectric becomes too thick, the polarization of the ferroelectric becomes zero.

Note that the same is concluded/predicted by the QSN theory as well. However, the underlying philosophy is completely different. The comparison is illustrated in Fig. 4. The QSN theory assumes the maximum in the Landau energy landscape is a physically accessible as well as stabilizable state. The depolarization field that appears in a FE-DE stack pushes the FE towards that maximum (Fig. 4a) and keeps it stable on top of the barrier. In the physical sense, when the centrosymmetric position is stabilized, it would correspond to a single-well potential for a particle vibrating around the centrosymmetric position and not by a double-well. This single-well is describing the dynamics of a (high-k) dielectric system and not a ferroelectric/double-well system: the flatter the single-potential well, the lower the vibrational frequency, therefore higher the dielectric response of the material. In essence, referring to the QSN as a misnomer for the high-k

dielectric suggests an oversimplified interpretation that doesn't fully capture the complexities of the material behavior.

In the transition-state theory on the other hand, the depolarization field pushes the hysteron towards both minima such that they have a 50-50 occupation (Fig. 4b). Equal occupation of states gives a net zero polarization according to equation 7, though switching of individual hysteron is by definition hysteretic [14]. In addition, the barrier does not define the "capacitance", instead it defines the likelihood of jumping of the hysteron from one state to another.

VI. CONCLUSION

Landau phenomenological model for phase transition is widely accepted. A particular way of interpreting the model predicts the existence of quasi-static negative capacitance (QSN). Specifically, the assumption that the barrier region in between two minima of the Landau potential is stabilizable thermodynamic state leads to such prediction. However Landau model is not a singular model for describing ferroelectricity while other available mathematical models do not predict the existence of QSN. We showed the Landau model originates from first principles and when interpreted in terms of transition-state-theory, unifies different available models of ferroelectrics. Doing so also shows QSN is not intrinsic to the Landau model rather it depends on the interpretation.

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