Conditions for Domain-Free Negative Capacitance

Prasanna Venkatesan Ravindran, *Graduate Student Member, IEEE*,
Priyankka Gundlapudi Ravikumar, *Student Member, IEEE*,
and Asif Islam Khan, *Senior Member, IEEE*

***Abstract*— While negative capacitance (NC) has been demonstrated in ferroelectric-dielectric (FE-DE) heterostructures in the form of capacitance enhancement, all experimental evidence, to date, suggests the existence of domains therein. Here, we address the question: what are the conditions to achieve ideal, domain-free NC in FE-DE heterostructures? Our main claim is that for given thicknesses of the ferroelectric and the dielectric layers, there is a critical value of domain wall energy parameter—above which the system would be stabilized in an ideal and robust domain-free NC state and would be robust against domain formation. Our analyses suggest that to achieve ideal NC, efforts should lie in understanding the means to control the domain wall energy on all fronts, both theory and experiments via high throughput design, discovery, and engineering of ferroelectrics.**

***Index Terms*— Domain wall energy, ferroelectric-dielectric (FE-DE) heterostructure, multi-domain, negative capacitance (NC).**

I. Introduction

NEGATIVE capacitance (NC) is an unstable state in a ferroelectric material in which the changes in the dielectric polarization (P) and the electric field (E) can occur in opposite directions [1]. Based on the Landau-Devonshire theory of ferroelectricity, a ferroelectric NC state can be stabilized in a ferroelectric-dielectric (FE-DE) heterostructure. When a ferroelectric thickness t_F is smaller than a critical value $t_{F,c}$ for a given dielectric thickness t_D, the depolarizing field due to the dielectric layer can drive the ferroelectric layer into a homogeneous, zero polarization ($P = 0$), NC state (Fig. 1). Such a state minimizes the free energy of the FE-DE heterostructure. In doing so, the ferroelectric layer can passively amplify the voltage at the FE-DE interface and enhance the capacitance of the composite structure above that of the constituent dielectric layer. However, it has long been known that such a heterostructure can also exist in a multi-domain, ferroelectric state [2], [3], [4], [5], [6]. One of the early debates on this topic has been whether the formation of a domain pattern precludes the NC response from the ferroelectric layer. This debate was put to rest after Zubko et al. [7] experimentally demonstrated capacitance enhancement in a multi-domain, perovskite-based FE-DE heterostructure, followed by observation of local regions of negative dielectric permittivity in polar vortices and skyrmions [8], [9].

That being said, the answer to the question, whether a ferroelectric layer can exist in a globally stabilized, zero polarization ($P = 0$), NC state in an FE-DE structure lacks clarity. Such a state has neither been experimentally demonstrated nor been studied theoretically in sufficient detail. NC in a

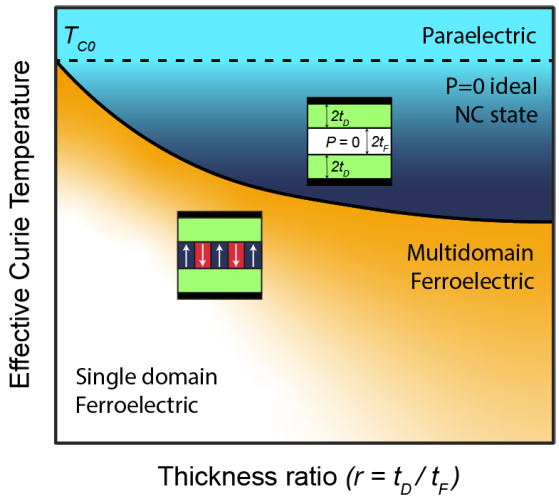

Fig. 1. Phase plot of effective Curie temperature as a function of the thickness ratio r. The black curve shows the transition from a homogeneous zero-polarization, NC state to a multi-domain ferroelectric state in an FE-DE heterostructure. Despite several experimental efforts, the former has remained elusive leading to questions about the existence of such an ideal NC state. This letter analyzes the conditions on the domain wall energy parameter D for which the zero-polarization state becomes energetically more favorable than the multi-domain state at a given operating temperature. T_{C0} is the Curie temperature of the standalone ferroelectric material above which the material is paraelectric. t_D and t_F stand for the dielectric and ferroelectric thickness, respectively, while P represents the polarization.

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Prasanna Venkatesan Ravindran and Priyankka Gundlapudi Ravikumar are with the School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332 USA (e-mail: pravindran6@gatech.edu).

Asif Islam Khan is with the School of Electrical and Computer Engineering and the School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332 USA.

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multi-domain scenario has recently been theoretically analyzed in [10], [11], [12] and [13]. Hoffmann et al. [12] showed a homogeneous, $P = 0$, NC state can exist if the lateral dimensions of the heterostructure is constrained below a critical limit. Rollo et al. [14] presented a case for the stabilization of NC in metal-ferroelectric-dielectric-metal (MFDM) structures, emphasizing the importance of the quality of the FE-DE interface. Despite these works making earnest attempts to address the problem, the integration of the Landau-Ginzburg-Devonshire framework with the electrostatics of FE-DE heterostructures is known for mathematical inconsistencies stemming from models not being self-consistent. Phase-field simulations have been used to address these inconsistencies and Saha and Gupta [11] took into account the spatial variation of polarization within a domain and explained the crucial role of domain wall energy in stabilizing a homogeneous, zero polarization state ($P = 0$) with NC in such heterostructures using phase-field simulations.

In this work, we address this question by using a model for a multi-domain FE-DE heterostructure presented in [15] based on the electrostatics of the multi-domain state at temperatures close to the Curie temperature T_{C0}, where the heterostructure transitions from a ferroelectric to a paraelectric phase. In FE-DE heterostructures, the effective Curie temperature T_C' decreases as the volume fraction of the dielectric layer is increased. For a given heterostructure, at temperatures between T_{C0} and T_C', the homogeneous, zero polarization, NC state is stabilized before the heterostructure transitions to a multi-domain ferroelectric state below T_C' (Fig. 1). Our key result is that for a given FE-DE heterostructure with ferroelectric thickness $t_F < t_{F,C}$ and operating temperature T_{op}, there exists a critical domain wall energy required to stabilize the ferroelectric layer in this zero polarization, NC state. Above this critical energy, the system is bound to be stable in this state irrespective of the length scale of the sample in the lateral dimensions.

II. Single Domain Scenario in Ferroelectric-Dielectric Heterostructure

We first review the concept of the critical ferroelectric thickness $t_{F,C}$ in an FE-DE heterostructure in the single domain scenario as originally described in [1]. The free energy density per unit volume of a ferroelectric U_F can be expressed as an even order polynomial of P–*i.e.*, $U_F = \sum_{i=1,2,\ldots} \alpha_i P^{2\cdot i}$ where α_i are anisotropy constants. For the sake of simplicity, we assume that the ferroelectric material exhibits a first-order phase transition–*i.e.*, $\alpha_1 = 1/2\epsilon_F(T)$ where $\epsilon_F = M/(T - T_{C0})$ based on the Curie-Weiss law and $\alpha_i > 0$ for $i > 1$. Here, M and T_{C0} are the Curie constant and the Curie temperature, respectively. The free energy per unit volume of a dielectric layer is represented by a single well energy landscape $U_D = D_D^2/2\epsilon_D$, with D_D and ϵ_D being the electric flux and the dielectric permittivity of the dielectric layer. Equating D_D to P, the energy density of the heterostructure is given by

$$U = \frac{t_F U_F + t_D U_D}{t_F + t_D} = \frac{1}{2\epsilon'(T)} P^2 + \sum_{i=2,\ldots} \alpha_i P^{2\cdot i} \quad (1)$$

TABLE I
Material Parameters for the Ferroelectric and the Dielectric Layers

Parameter	Value
Dielectric layer	
Dielectric permittivity ϵ_D	$300\epsilon_\circ$
Ferroelectric layer	
Out-of-plane permittivity $\epsilon_\perp$	$120\epsilon_\circ$
Curie temperature T_{C0}	1244 K
Curie constant M	4.1×10^5 K $\times\epsilon_\circ$
In-plane permittivity $\epsilon_\parallel$	M/T_{C0}
Domain wall half width ξ_0	0.5 nm

where ϵ' is the effective dielectric constant of the heterostructure. ϵ' has the same functional form as that of ϵ_F, with T_C replaced by an effective Curie temperature T_C', given as

$$T_C' = T_C - \frac{M}{\epsilon_D} r \quad (2)$$

where r is the ratio between the thicknesses of the dielectric and the ferroelectric layers ($r = t_D/t_F$). At an operating temperature T_{op}, the $P = 0$ state will be stable if $T_C' < T_{\text{op}} < T_{C0}$. For a given α_i and $T_{C0} > T_{\text{op}}$, the effective Curie temperature is lower than the operating temperature if $t_F < t_{F,C} = Mt_D/(T_{C0} - T_{\text{op}})\epsilon_D$. This implies that for $t_F < t_{F,C}$, the ferroelectric will be stable in the $P = 0$ state.

III. Multi-Domain Scenario in Ferroelectric-Dielectric Heterostructure

We now consider the multi-domain scenario. We assume that each FE layer of thickness $2t_F$ is sandwiched between two DE layers each with a thickness of $2t_D$. The electrostatics of this system close to the transition temperature has been adapted from [15]. We modify the (2) in [15] to introduce a unit-less proportionality constant, the domain wall energy parameter D as a measure of the domain wall energy in the multi-domain state resulting in the domain wall energy term being $D^2\xi_0^2\nabla^2 P$. A higher D implies a higher domain wall energy and a higher threshold for forming domains while a lower one corresponds to a lower domain wall energy which would make domain formation easier. Taking into consideration the domain wall energy, the z component of the polarization in the ferroelectric layer P is given by the non-linear Ginzburg-Landau equation

$$(T/T_{C0} - 1)P + P_0^{-2}P^3 - D^2\xi_0^2\nabla^2 P = \frac{\epsilon_\parallel}{4\pi} E_z^{(f)}. \quad (3)$$

Following a similar approach, we obtain the effective Curie temperature T_C' of the FE-DE heterostructures numerically. The effective Curie temperature is defined as the highest temperature at which a domain width (in turn, a domain configuration) is defined.

The FE and DE material parameters as used in this work are based on a $PbTiO_3/SrTiO_3$ heterostructure and are listed in the Table I [7]. Over the last decade, works have reported perovskite-structured FE-DE superlattices with individual ferroelectric layers as small as a few unit cells [7], [8], [9]. Simultaneously, perovskite structure ferroelectrics also have been scaled down to below 10 nm [16], [17]. While the model

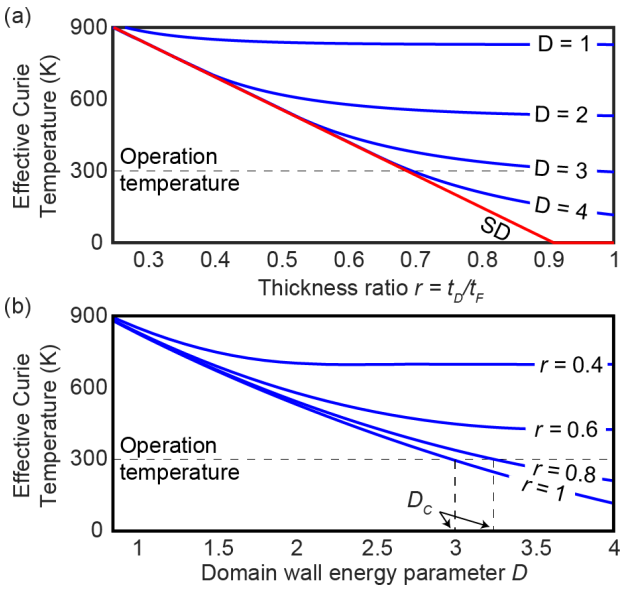

Fig. 2. Variation of effective Curie temperature (a) with thickness ratios for different D and (b) with domain wall energy parameters for different r in FE-DE heterostructures with $t_F = 5$ nm. As D is increased, the effective Curie temperatures of multidomain heterostructures (blue) approach the effective Curie temperatures calculated from the single domain, homogeneous polarization model (red).

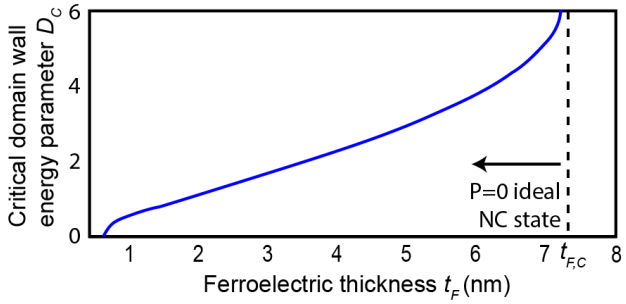

Fig. 3. For a given $t_F < t_{F,C}$ there exists a critical domain wall energy parameter D_C above which the system is in a stable zero-polarization NC state at an operating temperature of 300 K and for $t_D = 5$ nm. While D is an intrinsic property, the critical domain wall energy parameter D_C depends on the thickness of the ferroelectric and is not an intrinsic property.

is valid for any thickness range, in this work, we consider FE-DE superlattices with alternating layers of ferroelectric and dielectric with $t_F = 5$ nm.

For a fixed domain wall energy parameter D, the variation of the effective Curie temperature with the thickness ratio of dielectric to the ferroelectric is shown in Fig. 2(a). For lower values of D, the T_C' saturates closer to the T_{C0}. As D is increased, the curves approach the behavior of a domain-free ferroelectric system (red curve) as domain formation is made unfavorable by the increasing domain wall energy. The operating temperature is assumed to be the 300 K in this work. The decreasing T_C' with increasing D shows that for suitable D, the FE-DE structure would be stabilized in a $P = 0$, NC state at the operating temperature. Fig. 2(b) shows variation of T_C' with the D for different dielectric thicknesses. We observe that T_C' decreases with increasing D. For $t_F < t_{F,C}$(equivalently, $r > r_C$), there is critical domain wall energy parameter D_C at which $T_C' < T_{\text{op}}$ indicating that the ferroelectric will be stabilized in a zero-polarization, NC state as suggested in [1] at room temperature for $D \geq D_C$.

The critical domain wall parameter D_C is a function of the dielectric properties of the ferroelectric material and the ferroelectric and dielectric thicknesses. Based on the material parameters, we obtain $t_{F,c} = Mt_D/(T_{C0} - T_{\text{op}})\epsilon_D = 7.24$ nm. For a given t_D and $t_F < t_{F,C}$, there exists a minimum domain wall energy required to stabilize the ferroelectric in a single domain, homogeneous $P = 0$, NC state. Fig. 3 shows the variation of the critical domain wall energy parameter D_C with the ferroelectric thickness t_F for $t_F < t_{F,C}$.

Recent studies have reported that HfO_2 exhibits a negative domain wall energy ($f_{dw} = -18$ mJ/m^2) for 180° domains, making the formation of these domains infinitely easy [18]. However, since D_C is always positive, it is not possible to stabilize HfO_2 layers dominated by these domain walls in a $P = 0$ ideal NC state in an FE-DE system, regardless of the dielectric and ferroelectric thickness. Nevertheless, NC effects have been experimentally observed in fluorite-type ferroelectric systems such as HfO_2 in previous studies, indicating that the current understanding of these materials may be insufficient for exploring NC at the nanoscale [19], [20], [21]. Moreover, practical HfO_2 contains multiple domains with about ten types of 180° and 90° domain walls within a single grain, which presents exciting opportunities for exploring the physics of NC in these materials [22], [23], [24].

Research focused on domain wall energies and domain wall widths for different materials in different superlattices and under different stress and mechanical boundary conditions can offer valuable insights into the pathways for stabilizing the single-domain zero-polarization NC state. For example, HfO_2 has a domain wall energy of -18 mJ/m^2 and a domain wall width of 2.5 Å [18] while strained $PbTiO_3$ on $SrTiO_3$ substrates and KNO_3 on $KTaO_3$ substrates have domain wall widths of 1 and 1.2 nm respectively at low-temperatures [7], [15]. However, this database is currently limited, and expanding it to encompass a broader range of materials would be a valuable pursuit.

IV. Conclusion

In conclusion, we have analyzed the possibility of a zero-polarization, NC state in FE-DE heterostructures using numerical results from a multi-domain model of the heterostructure. We show that for a given thickness of the dielectric and ferroelectric layers, there exists a critical value of the domain wall energy parameter only above which a single-domain zero-polarization, ideal NC state becomes stable. This points toward the need for further exploration of the energetics of domain walls and other functional materials like antiferroelectrics to achieve an ideal stabilized NC that can potentially lead to ultralow power transistors.

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