Electrical imprint effects model for low range THz transmittance spectrum in ferroelectric films

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Tunable transmittance response in the 0.1 – 3.5 THz range for a lead Zirconate Titanate Ferroelectric film under imprint effects and surface anisotropy is calculated by adapting the classical Landau Devonshire theory and the Rouard’s method. Induced electrical field is introduced by shifting the \( P - E \) polarization profile, while the dielectric permittivity frequency dependence enters into the formalism by taking into the account the soft phonon mode \( E(01) \) contribution in the framework of the Drude-Lorentz model. It is found that two optical states of light transmittance are closely correlated with the imprint strength at zero applied field and normal incidence for direct and inverse polarization.

**Keywords:** Multiferroics, Transmittance, Index of refraction, imprint, Ferroelectric film, Terahertz

I. Introduction

Electrical imprint is generally considered as an undesirable effect in FeRAM technology mainly because it attempts against the data storage stability [1]. Nevertheless, electrical imprint treatments on ferroelectric arrays have rise special interest in the last decade since they have demonstrated a crucial role in the design of the shape of non-volatile memories in piezoelectric actuators [2]. Physical origin of imprint is sill under debate, although the ferroelectric degradation of polarization properties associated to non switching surface layers with a large residual field in the electrode-ferroelectric frontier has been identified as one responsible mechanism for the shifting in the hysteresis loop [3], [4]. Imprint control can be achieved by exposing the sample during long periods and high temperatures [5] or by injecting electronic charges into the electrode-ferroelectric interface via Schottky thermoionic current [6]. First procedure has been successfully implemented in experimental lead zirconate titanate (PZT) optical shutters with stable performance on its dielectric susceptibility response after a long range of commutation pulses (\( \sim 10^5 \)) [7], [8], outlining an alternate principle on light transmittance devices. Advances in the THz limit technology have also found promising proposals for low power operation on hybrid ferroelectric/graphene layer nanoplasmonic waveguides [9], [10]. In this paper, we introduce the electrical imprint strength as an essential mechanism for the observed offset in the characteristic hysteresis \( P(E) \) loop, and calculate the effective index of refraction, the optical transmittance and the shape of memory under typical applied fields up to 300 kV/cm for 800 nm PZT systems in the edge of low THz. It is shown that a two-optical asymmetric states of light transmittance can be achieved by manipulating the strength of a vertical or horizontal imprint at zero field, in agreement with recent experimental reports [8].

II. Transmittance Response Model

The classical Landau-Ginzburg-Devonshire (LGD) model [11], [12], [13] provides the description for the polarization field distribution \( P(z, E) \) in ferroelectric (FE) phase under applied electric field \( E \). The single component for the polarization field \( P(z, E) \) is obtained by solving the third order non-linear differential equation:

\[
-\alpha \xi_b^2 \frac{\partial^2 P}{\partial z^2} + \alpha P + \beta P^3 = E \cdot \hat{n},
\]

(1)

where \( \alpha \) and \( \beta \) are the typical parameters taken from the renormalized Gibbs free energy functional in the \( \epsilon \)-phase configuration [11]. \( \xi_b \) corresponds to the correlation length in FE state and \( E = E \cdot \hat{n} \) defines the relative (and uniform) electric field intensity along \( z \)-direction. The polarization field distribution profile nearby the surface of a ferroelectric film of thickness \( \ell \) changes with its perpendicular distance as

\[
\left( \frac{\partial P}{\partial z} \right)_{z=0,\ell} = \pm \lambda^{-1} P(z = 0, \ell),
\]

(2)

in agreement with the Kretschmer’s theory [14]. \( \lambda \) encodes the asymmetric depolarization field effects due to a large variety of phenomena, among others, the relative orientation of \( P \) respect to the normal of the surfaces, the proximity vacuum-interface boundary depletion field or the mismatch strain for samples in contact with a substrate [15]. In the frame of a linearized approach, the complete polarization profile is constructed by writing \( P \approx (P(E)) + \delta P(z, E) \), where \( (P(E)) \) is taken as the average polarization of the film calculated from [1], and \( \delta P(z, E) \) corresponds to the fluctuations around \( (P(E)) \). Therefore, \( \delta P \) must satisfy:

\[
-\alpha \xi_b^2 \frac{\partial^2 \delta P}{\partial z^2} + \bar{\delta} P = E,
\]

(3)

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with $\tilde{\alpha} = \alpha + 3\beta(P(E))^2$. The solution for $P(z, E)$ with the boundary conditions [2] is given explicitly by:

$$P(z, E) = H(E) \left( 1 + F(E) \cosh \left( \frac{2z - \ell}{2\xi_b} \right) \right),$$  \hfill (4)

where $H(E) = \langle P(E) \rangle + \tilde{\alpha}^{-1} E$ and the structure factor $F(E)$ takes into account the characteristic lengths in the system, namely, the thickness $\ell$, the surface depletion $\lambda$, and the renormalized coherence length in the FE state $\xi_b(E) \equiv \xi_b = \xi_b \sqrt{\alpha / \tilde{\alpha}}$, which depends on the transition temperature $T_C$ and the external field intensity. The dependence for the average polarization $\langle P(E) \rangle$ must be obtained self-consistently [17]. Factor $F(E)$ is calculated as $F^{-1}(E) = -\left[ \cosh \left( \ell/2\xi_b(E) \right) + (\lambda/\xi_b(E)) \sinh \left( \ell/2\xi_b(E) \right) \right]$. By inserting the adjustment correlations in terms of the coercive field $E_c$ and the remnant polarization at zero field $P_r$ as [18] $|\alpha| = 3\sqrt{3}E_c/2P_r$, and $P_r = \sqrt{|\alpha|/\beta}$, the expression for the dielectric susceptibility $\chi(E)$ as an intrinsic function of applied field $E$ in the framework of the Landau-Khalatnikov theory is derived [19]:

$$\chi(E) = \frac{2P_r^3}{3\sqrt{3}E_c(P_r^2 + 3(P(E))^2)}. \hfill (5)$$

Hence, the index of refraction $n_\omega(z, E)$ is given by [20, 21]:

$$n_\omega(z, E) = n(\omega) \left[ 1 + Q(z, E) \right]^{1/2}, \hfill (6)$$

with $Q(z, E) = \chi(E) \left[ 1 + F(E) \cosh \left( (2z - \ell)/2\xi_b(E) \right) \right]$. The correlation with the phase difference associated to the optical path traveled by a coherent electromagnetic wave for those spatially inhomogeneous systems is defined as [22]:

$$\delta = \frac{\omega}{c} \int_0^\ell n_\omega(z, E) \, dz = \frac{\omega}{c} \tilde{n}_c(\omega, E), \hfill (7)$$

where $\tilde{n}_c(\omega, E) \equiv \tilde{n}_c$ is taken as the effective value for the index of the refraction in the length $\ell$:

$$\tilde{n}_c = n(\omega) \kappa_1^{-1} \left[ 1 + Q(\ell/2, E) \right]^{1/2} \mathcal{E}(\kappa_1 | \kappa_2), \hfill (8)$$

$\mathcal{E}(\kappa_1 | \kappa_2)$ represents the incomplete elliptic integral of the second kind [23] with $\kappa_1 \equiv \kappa_1(E) = i\ell/4\xi_b(E)$ and $\kappa_2 \equiv \kappa_2(E) = 2F(E) \chi(E) / \left[ 1 + Q(\ell/2, E) \right]$. Far infrared dielectric response of Lead (Zirconate) Titanate (PT-PZT) have been intensively investigated by using the classical Drude-Lorentz type model in the THz range [24, 25, 26]:

$$\varepsilon(\omega) \sim \varepsilon_{\text{THz}} + \frac{\Delta\varepsilon_{\text{THz}} \omega_M^2}{\omega_M^2 - \omega^2 + i\omega}; \hfill (9)$$

where $\omega_M \sim 1.6$ THz and $\Delta\varepsilon_{\text{THz}} = 150$ corresponds to the adjusted frequency of the phononic $E$ (TO1) soft central mode selected for (undoped) PZT films [27]. Its relationship with the factor $n(\omega)$ in Equation (5) is given by $n(\omega) = \sqrt{\varepsilon(\omega)}$. Two Debye relaxation mechanisms are present in the permittivity response model, however, they lie into the GHz range and do not have significant effects on the transmittance spectrum in the interval of interest. The transmittance response $T(\omega, E) \equiv T_\omega = \text{abs}[\tilde{x}]^2$ is calculated by using the Rouard’s method for normal incidence as a function of the phase difference $\delta$, the film index $\tilde{n}_c$ and its environment $n_0$ [28, 29]:

$$\tilde{\tau} = \frac{i\tilde{P} e^{-i\delta}}{(1 - \tilde{r}^2 e^{-2i\delta})}, \hfill (10)$$

$\tilde{P} = (\tilde{n}_c/n_0) \tilde{P}$ and $\tilde{r} = (1 - \tilde{n}_c/n_0)(1 + \tilde{n}_c/n_0)^{-1}$. Equations (7)-(10) constitute the core results in this paper: the transmittance spectrum due to the propagation of electromagnetic (THz) radiation in a ferroelectric film under vertical and horizontal imprint effects. Numerical results are discussed in the next section.

**III. Numerical Results**

Electrical polarization induced by imprint treatment has been qualitatively set into the formalism in terms of the saturation $P_s$ and coercive fields under the adjustment $P_s(E) = yP_s + P_s \tanh \left[ A(E \pm E_c - xE_c) \right]$, with $A = \tanh^{-1}(P_s/P_c)/E_c$ [30, 31, 32]. Parameter $y$ might encode the relative vertical imprint strength, and its negative value $y$ indicates that imprinting treatment has been perform by inducing an external polarization field in opposite direction of $P_s$. Figure [1] compares the hysteresis profile for a symmetrical loop without imprint treatment (black line), its vertical shifting under imprint effects for $y = +0.5, x = 0$ (red line) and the characteristic bias for $y = 0, x = +0.5$. Five regimes are readily identified: (I) direct polarization for positive
When non-imprinting procedure has been taken into account, the hysteresis loop remains symmetrical around $P = 0$ axis, and the bi-state optical transmittance mode vanishes. The spectrum exhibits a symmetrical butterfly shape with minimal transmittance peaks at $\pm E_c$. In case (b) $x = +0.5, y = 0$, the spectrum is horizontally biased and two states of light transmission emerges at zero field depending on the path of the polarizability ($I$) or ($III$). The minima of $T(E)$ remain symmetrical around its crossing point (identified as the electrical field value for which the transmittance function gets the same value for direct and inverse polarization), with higher values compared with the case (a). Curve (c) is calculated for $x = 0$ and $y = +0.5$. The crossing point is shifted for negative values of the externally applied field, the spectrum shows the maximum difference for the transmittance levels at $E = 0$, indicating that a stronger optical response arises when the vertical imprint treatment predominates. Figure [3] shows the evolution of the transmittance spectrum at fixed frequency (0.1 THz) for independent values of $x$ and $y$ in the range between $-3.5; 3.5$ and $-1.5; 1.5$ respectively, with the largest difference around 0.75 (labeled in open circles) at $y \sim 0.58$. Figure [4] illustrates the transmittance response for different imprint strengths from up to 3.5 THz in the far infrared edge (FIR). Solid lines represent the response in direct polarization state, while dashed lines are associated to depolarized states in the sample (lines (I) and (III) in the hysteresis cycle, respectively). The transmittance overlaps their lines regardless its polarization bias for $x = 0$, but it takes two values depending on the cycle history when imprint effects have been included into the calculations. Figures [6] show the contour lines in the transmittance response for simultaneous ($x, y$) imprint strengths in two different paths of
polarization. On the process \( V \rightarrow I \rightarrow II \) the response changes monotonously from 0.65 to 0.9 in contrast with the remarkable fluctuations resulting after calculating upon the \( III \rightarrow IV \) trajectory. Optical transmittance differences at zero field \( \Delta T = |T_{V \rightarrow I \rightarrow II} - T_{III \rightarrow IV}| \) for direct and inverse polarization states as a function of the positive imprint strength \( y \) and various frequencies in the THz regime are shown in Figure (6). Non shape memory effect is available without imprinting treatment \( (y = 0) \). \( \Delta T \) response is sensitive to the external radiation frequency since it tends to increase as the frequency approaches to the edge of the far infrared regime \( (\sim 0.1 \text{ THz}) \). The E(T01) phonon mode contribution becomes significant in the range between 1 to 3 THz, as referred in the \( 0 < y < 0.3 \)-crossover.

**IV. Concluding Remarks**

The explicit relationships for the effective index of refraction \( \hat{n}_e \) and the transmittance response \( T_\omega \) in ferroelectric films with surface anisotropy and induced electrical imprint are calculated by recasting the LGD model. It is shown that the transmittance spectrum is highly sensible under imprint strength in the edge of Terahertz range and depolarizing regime. Our approach is solely focused on vertical \( P(E) \) hysteresis loop displacement, although the model can be directly extended for asymmetrical slanted loops, resembling recent experiments reported for PZT films under Ba\(^{+2}\) (Sr\(^{+2}\)) modifications of dopant concentration in Pb sites \[34\], broadening a wide set of possibilities in electrochemical control on remnant polarization, coercive field and piezoelectric response in these ceramic materials. \( P(E) \) in equation \[4\] might be solved exactly, the line becomes slightly different compared with the proposed hyperbolic profile, but this procedure does not change in significant way the main behavior on the transmittance response. Detailed studies on the role of Zr/Ti compositional variation in PZT films have also demonstrate a close correlation between critical temperature \( T_C \), the short-long structural order crossover passing through rhombohedral-morphotropic phase boundary (MPB)-tetragonal phases, and piezoelectric activity in Lead Titanate system \[35\],\[36\],\[37\],\[38\], recalling the pertinence of LGD model for transitional states, specifically in its characteristic length \( \bar{\xi}_b \rightarrow \bar{\xi}_b (T_C) \). Transmittance measurements in ferroelectric thin film structures allow to perform indirect adjustments to Drude-Lorentz model \[9\] on its soft mode \( \omega_M \rightarrow \omega_M (E) \) and damping \( \gamma \rightarrow \gamma (E) \) parameters as the dielectric permittivity changes up to 10% for \( E \sim 100 \text{ kV/cm} \) \[39\] and 65%
Long-lasting imprint exposure in ferroelectric films, their intrinsic loss of polarization and retention effect acquire relevance in this scenario, and it constitutes an important issue that shall be considered on further investigations.

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