Abstract. We consider ferroelectric phase transitions in both short-circuited and biased ferroelectric-semiconductor films with a space (depletion) charge which leads to some unusual behavior. It is shown that in the presence of the charge the polarization separates into ‘switchable’ and ‘non-switchable’ parts. The electric field, appearing due to the space charge, does not wash out the phase transition, which remains second order but takes place at somewhat reduced temperature. At the same time, it leads to a suppression of the ferroelectricity in a near-electrode layer. Influence of the depletion charge on thermodynamic coercive field reduces mainly to the lowering of the phase transition temperature, and its effect is negligible. The depletion charge can, however, facilitate an appearance of the domain structure which would be detrimental for device performance (fatigue).

INTRODUCTION

Ferroelectric perovskite materials used in memory applications usually behave as semiconductors [1]. It is expected, therefore, that at the metal-ferroelectric contact a depletion zone and the corresponding (depletion) charge distribution is formed, similar to the situations with usual semiconductor-metal contacts. The corresponding electronic structure and related effects were extensively discussed for layered metal-semiconducting ferroelectric systems [2–8]. The depletion effects are especially important in switching devices [6]. The semiconducting behavior of some common ferroelectrics (PZT) was exploited in a series of papers [9–11] to account for some specific features of switching, fatigue, and rejuvenation phenomena in ferroelectric thin films.

The idea of possible importance of the depletion charge for the properties of thin ferroelectric films seems fairly natural. However, as will be shown below, ferroelectric properties in those systems are very peculiar. The consistent treatment demonstrates, in particular, that the effect of the depletion charge on thermodynamic coercive field is minute. This is a consequence of long-range Coulomb
(depolarizing) field which appears simultaneously with the inhomogeneous polarization. The depolarizing field makes the problem of finding the polarization field and the point of phase transition non-local, and the local, to a considerable extent, global dielectric response rigid. The effects of the depolarizing field were apparently neglected by the previous authors, Refs. [9–11]. Therefore, their general relevance is questionable because, as is shown below, the depolarizing field plays crucial role in determining the dielectric response and the very character of the phase transition. The depolarizing field leads to some important phenomena, like lowering of the critical temperature, $T_c$, possible monodomain-polydomain transition, etc.

In the present paper we describe the properties of ferroelectric films with the depletion charge in terms of the phenomenological Landau-Ginzburg-Devonshire (LGD) theory of ferroelectricity (see, e.g. [12]). We restrict ourselves to the case of a ferroelectric film with a polar axis perpendicular to the film plane. The intrinsically second-order ferroelectric in considered as a starting point. It is assumed that the charge distribution remains the same both in the paraelectric and the ferroelectric phases.

The key point in our treatment is that the polarization is divided into built-in (non-switchable) and ferroelectric (switchable) parts. Within the paper this division is mathematically strict: the built-in polarization, $P_b(r)$, corresponds to an extremum of the LGD thermodynamic potential. The extremum corresponds to a minimum in the paraelectric and a maximum in the ferroelectric phase. The latter is similar to a zero polarization solution for a pure short-circuited crystal. Such a solution corresponds to a maximum of the LGD free energy, whereas the physical solution corresponds to a minimum of the LGD free energy and a finite (spontaneous) polarization. We shall call the ferroelectric polarization the difference

$$P_f = P - P_b. \tag{1}$$

The ferroelectric polarization is switchable: there always are two equivalent solutions for $P_f(r)$ in the ferroelectric phase. In the case of a non-zero bias we include the change of the polarization due to the bias into $P_f$, whereas the built-in polarization remains unchanged.

It is convenient to start with a short-circuited film of a linear dielectric with a homogeneous density of the space charge, $\rho$. The electric displacement $D$ in the film is given by the electrostatic equation $\text{div} \vec{D} = \rho$, or simply

$$dD/dz = \rho = \text{const}, \tag{2}$$

where $z$ is the coordinate perpendicular to the film plane. Taking into account that the voltage across the short-circuited film is zero, one finds:

$$D = (z - d/2)\rho. \tag{3}$$

From
\[ D = \varepsilon_0 E + P, \quad (4) \]

and
\[ D = \varepsilon\varepsilon_0 E, \quad (5) \]

one obtains for the polarization \( P \):

\[ P = \frac{\varepsilon - 1}{\varepsilon} D. \quad (6) \]

Now we shall consider a ferroelectric in a paraelectric state. We shall neglect, for a moment, the nonlinearities and make some qualitative remarks. It follows from Eq. (6) that \( P \approx D \) when \( \varepsilon \gg 1 \). Note that the electric displacement is always determined by the charge density, it does not depend on the dielectric constant [cf. (2)]. When the phase transition is approached, the dielectric constant increases, but the polarization remains practically unchanged, unlike the electric field which exhibits a strong temperature dependence. At the Curie temperature \( \varepsilon = \infty \) the field is zero in the linear approximation, while the polarization is almost the same as it was far from the transition. In other words it is more appropriate to talk about a built-in polarization rather than a built-in electric field while considering the effects of space charge in ferroelectrics. This conclusion is not limited, of course, to the case of homogeneous distribution of the space charge. For a medium with a large dielectric constant the value of the polarization is close to the value of the displacement field (6). Hence, near complete compensation of the space charge (produced by ionized donors, etc.) by the bound charges, corresponding to inhomogeneity of the polarization, occurs in a ‘soft’ dielectric medium (here ‘soft’ refers to medium with relatively large dielectric constant).

The difference between the ferroelectric and non-ferroelectric (built-in) polarization can be clarified by considering the effects of the bias voltage. One finds for a linear dielectric

\[ D = (z - d/2)\rho + \varepsilon\varepsilon_0 U/d, \quad (7) \]

where \( U \) is the bias voltage and the polarization \( P \) naturally splits into two parts, the switchable (‘ferroelectric’) polarization \( P_f \) and non-switchable (‘built-in’) polarization \( P_b \):

\[ P = P_f + P_b; \quad (8) \]

\[ P_f \equiv \varepsilon_0 (\varepsilon - 1) U/d, \quad (9) \]

\[ P_b(z) \equiv (z - d/2)\rho \frac{\varepsilon - 1}{\varepsilon}. \quad (10) \]

Thus, in the presence of both the space charge and the bias voltage, there are two contributions to the polarization, but only one of them ‘feels’ the phase transition.
The built-in polarization $P_b$ does not change with the bias, it remains inhomogeneous and almost insensitive to the phase transition [since $(\epsilon - 1)/\epsilon \approx 1$]. The induced (ferroelectric) polarization $P_f = (\epsilon - 1)\varepsilon_0 U/d \equiv (\epsilon - 1)\varepsilon_0 E_{\text{ext}}$ is homogeneous. The corresponding susceptibility $\chi_f \equiv dP_f/dE_{\text{ext}} \propto \varepsilon - 1$ diverges at the transition temperature in the linear approximation. We provide more details and discussion about the division of the polarization into ferroelectric and non-ferroelectric parts below.

**PHASE TRANSITION IN THE PRESENCE OF HOMOGENEOUS SPACE CHARGE**

**Main equations**

The nonlinear electric equation of state has a usual Landau form:

\[ AP + BP^3 = E, \tag{11} \]

where $P(E)$ are the $z$-components of the polarization (electric field). We assume, as usual:

\[ A = \alpha(T - T_c), \quad B = \text{const}, \tag{12} \]

where $T_c$ is the Curie temperature and $\alpha = \text{const} (\alpha, B > 0)$. Together with Eqs.(2),(4) and the boundary condition

\[ \int_0^d E dz = U, \tag{13} \]

we now have the complete set of equations to treat the ferroelectric phase transition in an electroded film. Note that we cannot use Eq. (7) now because it implies a linear relation between $D$ and $E$, whereas we are interested in a proper account for the non-linear effects.

Integrating Eq. (2), we find with the use of (4):

\[ \varepsilon_0 E(z) + P(z) = \rho z + K, \tag{14} \]

where $K$ is a constant which should be found from Eq. (13). We obtain:

\[ \varepsilon_0 E(z) = -P(z) + (z - d/2)\rho + \frac{1}{d} \int_0^d P(z) dz + \varepsilon_0 E_{\text{ext}}, \tag{15} \]

where the external field is produced by external bias voltage,

\[ E_{\text{ext}} = U/d. \]

Combining this with Eq. (11) we get:
\[(A + \varepsilon_0^{-1})P + BP^3 - \frac{1}{d\varepsilon_0} \int_0^d P(z)dz\]
\[= (z - d/2)\rho/\varepsilon_0 + E_{\text{ext}}.\]  \hspace{1cm} (16)

From Eqs. (16),(1) we obtain, up to terms \(\propto P^2_f\):
\[(A + 3BP_b^2 + \varepsilon_0^{-1})P_f + 3BP_bP_f^2 + BP_f^3\]
\[-\frac{1}{d\varepsilon_0} \int_0^d P_f(z)dz = E_{\text{ext}}.\]  \hspace{1cm} (17)

**Paraelectric phase**

Let us first calculate \(P_f\) in the paraelectric phase to the linear approximation, i.e. for small \(U\), neglecting the terms \(\propto P^2_f\) and higher. We have to solve the simple integral equation
\[(A + 3BP_b^2 + \varepsilon_0^{-1})P_f - \frac{1}{d\varepsilon_0} \int_0^d P_f(z)dz = E_{\text{ext}}.\]  \hspace{1cm} (18)

Introducing a notation
\[I \equiv \frac{1}{d\varepsilon_0} \int_0^d P_f(z)dz,\]  \hspace{1cm} (19)
we find from (18):
\[P_f = \frac{E_{\text{ext}} + I}{A + 3BP_b^2 + \varepsilon_0^{-1}}.\]  \hspace{1cm} (20)

To find \(I\) we substitute this expression into Eq. (19) and, as a result, find \(P_f\) in an explicit form:
\[P_f(z) = E_{\text{ext}} \frac{1}{1 - G} \frac{1}{A + 3BP_b^2(z) + \varepsilon_0^{-1}},\]  \hspace{1cm} (21)
where
\[G \equiv \frac{1}{d\varepsilon_0} \int_0^d \frac{dz}{A + 3BP_b^2 + \varepsilon_0^{-1}}.\]  \hspace{1cm} (22)

Thus:
\[1 - G = \frac{1}{d\varepsilon_0} \int_0^d \frac{A + 3BP_b^2}{A + 3BP_b^2 + \varepsilon_0^{-1}}dz \approx A + 3\langle P_b^2 \rangle,\]  \hspace{1cm} (23)
where \(\langle \ldots \rangle \equiv d^{-1} \int_0^d dz \ldots\), and we have taken into account that typically \(\varepsilon_0^{-1} \gg (A, 3BP_b^2)\).
We see, therefore, that the susceptibility $\chi_f = dP_f/dE_{\text{ext}} \propto (1 - G)^{-1}$ diverges at the temperature $\tilde{T}_c$, which is lower than the Curie-Weiss temperature $T_c$ in pure crystal without space charge, and the divergence of the dielectric response would take place when $A = -3B\langle P^2_b \rangle$, i.e. at $T = \tilde{T}_c$:

$$T_c - \tilde{T}_c = \frac{3B\langle P^2_b \rangle}{\alpha}. \quad (24)$$

Let us estimate this difference. For a displacive transition $B$ and $\alpha$ have normal ‘atomic’ values [12]. For $P_b \approx P_{\text{at}}$, where $P_{\text{at}}$ is the atomic polarization, $T_c - \tilde{T}_c$ would be about $T_{\text{at}} \sim 10^4 - 10^5 K$. For the charged impurity concentration $N_d$ one estimates $P_b \sim (N_d/N_{\text{at}})(d/d_{\text{at}})P_{\text{at}}$ where $N_{\text{at}}$ is the ‘atomic’ concentration $(10^{22} - 10^{23}) \text{cm}^{-3}$, $d_{\text{at}}$ is the ‘atomic’ distance (unit cell length, 3-5 Å) With the donor concentration $N_d = 10^{18} \text{cm}^{-3}$ [9], the thickness of the totally depleted film (equal the width of the depletion layer) would be about $2 \cdot 10^3 \text{Å}$, and we estimate $P_b \sim (10^{-2} - 10^{-3})P_{\text{at}}$ and $T_c - \tilde{T}_c \sim (1 - 100)K$. We see that the phase transition temperature can be reduced substantially, i.e. the paraelectric phase can be considerably ‘harder’ (dielectric response reduced) than the same phase in the pure crystal.

We see already that there is a radical difference between the effects of external field (the bias voltage) and the built-in field (polarization) on the ferroelectric transition. The former would smear out the phase transition and shift the maximum of the dielectric response to higher temperatures, while the built-in field does not lead to the maximum in the dielectric response at $A > 0$. It immediately follows from Eq. (21) that the only solution for $E_{\text{ext}} = 0$ is $P_f = 0$. This means that above the critical temperature the ferroelectric part of the polarization is zero, indicating that the built-in field has not washed out the transition. The ferroelectric susceptibility diverges as $(T - \tilde{T}_c)^{-1}$ in the vicinity of the phase transition. The exact nature of the phase transition is difficult to establish in general case, but the explicit solution below for a special case (space charge at the central plane) indicates that it remains second order. It is possible that the system may transform into a polydomain state before reaching $\tilde{T}_c$.

**Ferroelectric phase**

But what happens at $A < 0$? This is not so easy to determine. We shall try to answer this question, at least semi-quantitatively, but first we have to explain what the difficulty is. It is seen from Eq. (21) that $P_f$ is inhomogeneous over the sample, being smaller near the electrodes. It is worth mentioning that inhomogeneity of $P_f$ under the bias voltage is different from the inhomogeneity of the dielectric susceptibility of the paraelectric phase. Indeed, the ‘local’ dielectric susceptibility is what one would find by cutting out a small piece of the ferroelectric at a given position in the sample, making a capacitor out of this piece, and measuring its dielectric response. In our case we have to ‘fill up’ the capacitor with a medium
FIGURE 1. Schematic of the dielectric response $\chi_f^{-1} = dE_{ext}/dP$ which becomes inhomogeneous in the presence of the depletion charge (a), and the built-in polarization $P_b$ (b).

with a given local values of $P_b$: i.e. it is the built-in polarization that makes the ferroelectric response of the film effectively inhomogeneous. If $P_b$ were constant, the Eq. (18) would have had a homogeneous solution:

$$ (A + 3BP_b^2)P_f = E_{ext}. $$

One can see that the local susceptibility $\chi_{loc}(z) \equiv dP_f/dE_{ext} = (A + 3BP_b^2)^{-1}$ is more inhomogeneous than the polarization Eq. (21): one has to compare $3BP_b^2(z)$ in the case of $\chi_{loc}$, where $A$ is small, with $A + \varepsilon_0^{-1} \approx \varepsilon_0^{-1} >> A$ in the latter case. The smaller inhomogeneity of the polarization $P_f$ in relatively more inhomogeneous dielectric medium ($\chi_{loc}$) is due to the mutual Coulomb interaction of the bound charges (‘longitudinal’ inhomogeneity of the polarization). Consequently, the system tries to lower this energy by reducing the inhomogeneity. Along with the inhomogeneity of $\chi_{loc}$ there is also another inhomogeneity, which is described by the second term on the left hand side of the Eq. (17). It is expected to be important (if at all) well below the phase transition point, in the ferroelectric phase.

Since the problem of the film with depletion charge proves to be fairly complicated, it is instructive to consider first some special cases, where the treatment is easier, and get a feel of the relevant effects. The most natural way to simplify the problem is to replace the continuous distribution of the built-in polarization by a stepwise distribution. The simplest formal problem of that type would be a charge
located at a plane in the middle of the film with a constant charge density $\sigma$. This example allows an exact solution, important for the present discussion.

In this case the built-in polarization has opposite signs but the same absolute value in the two halves of the film, so that the film is homogeneously ‘hard’ (dielectric response is reduced). It is not completely homogeneous though, there is the inhomogeneity due to the second term on the left hand side of Eq. (17). But we can study now the effects of two inhomogeneities separately, beginning with the case where the linear inhomogeneity, given by the first term in the left hand side of Eq. (17) before $P_f$, is absent. There would be only a weaker quadratic inhomogeneity, given by the second term in Eq. (17) before $P_f^2$. We would expect that in this case the phase transition occurs into a monodomain state.

The explicit calculations [13] support this expectation. It proves out that the inhomogeneity of spontaneous value of $P_f$ ($P_{fs}$) is proportional to $P_{fs}^2$, i.e. it is obviously small near the phase transition. The inhomogeneity increases with decreasing temperatures, and a formation of domain structure becomes possible to compensate this inhomogeneity. However, according to the estimates, this formation is hardly possible in very thin films with nearly homogeneous distribution of the depletion charge which are of the main interest here. Therefore, it seems that the effects of the quadratic inhomogeneity can be neglected.

Since the phase transition takes place into homogeneous state the divergence of the dielectric response coincides with the phase transition temperature which is given by Eq. (24). Because of the lowering of the temperature the thermodynamic coercive field is also lower but this effect is very small. One finds [13]

$$\frac{\Delta E_c}{E_c} = \frac{9}{2} \left( \frac{P_0}{P_s} \right)^2 = \frac{9}{8} \left( \frac{\sigma}{P_s} \right)^2 = 0.02$$

where $P_s$ is the spontaneous polarization in the pure crystal and the estimations are made for the PZT film of the thickness $L = 300$ nm, the saturation polarization $P_s = 40 \mu C/cm^2$, and the donor concentration $N_d = 10^{18} cm^{-3}$, discussed previously [9].

Thus, we see that the effect of the depletion charge on the coercive field exists, but it is negligible. It has been speculated that the ‘experimental’ coercive field for nucleation $E_{cn}$ should be reduced by exactly the value of the built-in field $E_b$, $E_{cn} = E_{ext} + E_b$ [9–11]. Since these authors have estimated $E_b \approx 100kV/cm$, whereas the observed coercive field was $E_c \approx 80kV/cm$ [9], one would conclude that the coercive field has been suppressed by more than a half by the built-in field. However, this result and the whole previous analysis are rather questionable, since no actual nucleation processes have been considered in Refs. [9–11].

Now we shall discuss the effects of the linear inhomogeneity. Let us consider the case of two ‘hard’ near-surface charged layers, as depicted in Fig. 2. Such a distribution is more close to the usual case, Fig. 1. For $A + 3BP_0^2 > 0$ the system resembles a plate of a pure ferroelectric with two ‘passive’ layers close to the electrodes. Phase transitions in a similar system (ferroelectric plate with vacuum
FIGURE 2. Schematic of a ferroelectric film with two charged planes inside. The charged planes lead to piece-wise built-in polarization $P_b$.

gaps near the electrodes) were studied by Chensky and Tarasenko [14]. They found that there are transitions to both monodomain and polydomain states depending on geometrical parameters. Generalizing their consideration to the case of two dielectric layers we found that the transition to the monodomain state takes place if

$$d_1 < d_{1c} = \varepsilon_1 \left( \frac{12\varepsilon_0\kappa}{\varepsilon_\perp} \right)^{1/2},$$

(26)

where $d_1$, $\varepsilon_1$ are the width and the dielectric constant of the ‘passive’ layer, $\varepsilon_\perp$ is the dielectric constant in the plane of the film (perpendicular to easy axis). In our case the value of $d_{1c} \sim d$ can be estimated as:

$$d_1 \sim \frac{P^2_{at}}{P^2_0}d_{at} \sim (10^4 - 10^6)\text{Å}.$$  

(27)

This estimate is certainly crude but it suggests that the phase transition in completely depleted films proceeds into a monodomain state. We have recently discussed a domain structure in a ferroelectric plate with ‘passive’ layers [15]. It was found that far from the phase transition a domain structure exists for any passive layer of whatever thickness. Therefore, one can expect that a domain structure becomes energetically favorable at some temperature below the phase transition in
a short-circuited completely depleted ferroelectric film. This may be of crucial importance for the switching phenomena (and the fatigue) as it has been mentioned in [15].

CONCLUSIONS

We have demonstrated a peculiar nature of the phase transition in ferroelectric films with depletion (space) charge, and specific properties of the ferroelectric phase. The charge leads to appearance of the built-in (frozen) polarization which is not sensitive to the ferroelectric phase transition, and it suppresses the ferroelectricity in the near-electrode regions. The crux of the matter is that the system is strongly affected by long-range Coulomb field, accompanying the inhomogeneous polarization, which makes the local and, to some extent, the global dielectric response rigid (meaning the reduced dielectric susceptibility in comparison with pure system without space charge). The main effect is that it suppresses the critical temperature across the whole sample. The effects of the depolarizing field in this problem have been apparently neglected by previous authors [9–11], who also speculated about built-in field assisted switching in ferroelectric films. Since no actual nucleation processes have been considered in these works, we doubt those speculations have any justification.

The effect of the depletion charge on the nucleation and the fatigue is expected to be similar to that of near-electrode ‘dead’ layers discussed in Ref. [15].

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