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Model for ferroelectric semiconductors thin films accounting for the space varying permittivity

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Reducing thickness of ferroelectric films typically comes with an apparent degradation of their ferroelectric and dielectric properties. The existence of low-dielectric interfacial layers is often invoked to explain such behaviors. Much work has been done on modeling ferroelectric thin films by considering a ferroelectric layer between two layers with low dielectric constant. In these models it is necessary to introduce extrinsic parameters; the dielectric constant and the polarization are step functions of the depth inside the film. We have developed a model for ferroelectric semiconductors based on the inhomogeneous Landau–Devonshire theory, including surface effects. The local electric field is determined by solving Poisson's equation in which a differential permittivity replaces the dielectric constant. We have found that the hysteresis loops were strongly influenced by the correlation length. That point is discussed by examining the electric field, polarization, and differential permittivity profile inside the film. It is shown that the differential permittivity strongly decreases with the correlation length increases. That phenomena leads to high electric fields inside the film and especially close to the surface. As a consequence, an explanation for thin film ferroelectric properties can be given by invoking space charge density many orders of magnitude lower than those usually considered. © *2005 American Institute of Physics*.
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I. INTRODUCTION

Ferroelectric ceramic thin films are being extensively investigated for applications in nonvolatile memories. The electrical characterizations of MFM (metal ferroelectric metal) structures and their interpretations are key points in the understanding of such material properties. Numerous experimental results for bulk ferroelectric properties are explainable by the existence of a layer of low dielectric constant material at the surface. This phenomena has been described by Känzig[1] for whom the surface anomalies are due to the existence of a surface layer of high electric field. Merz[2] has pointed out that since the dielectric constant is highly nonlinear and field dependent, it would thus be possible for the dielectric constant to vary within the material. In ferroelectric materials, however, the ionic part of the dielectric constant drastically decreases with increasing electric field due to the increasing stiffness of the perovskite lattice.[3] Despite these previous remarks, the electric field and relative dielectric constant are generally assumed to be uniform for bulk ferroelectrics.

Many authors[4,5] have adopted an approach which consists of considering ferroelectrics as insulators with two nonswitching dielectric layers, one adjacent to each electrode, each layer having the same thickness and a low relative dielectric constant. Moreover, in these conditions the polarization and the electric field are not uniform inside the ferroelectric on the whole, but are uniform inside each layer.

Ferrolectrics like lead zirconate titanate (PZT) have usually been regarded as insulators, when their ferroelectric properties are discussed. The view point regarding thin ferroelectric film as a semiconductor seems to be confirmed by experiments. For example, a space charge layer at the metal ferrolectric contact was suggested by the current through ferroelectric metal structures, which showed the Schottky-like conduction.[6] Similarly, the space charge effect, i.e., Schottky barrier at the metal ferroelectric interface, is considered to be one of the mechanisms that intrinsically reduces the dielectric constant of very thin high dielectric films like PZT.[7–9]

Chai *et al.*[10] considered ferroelectrics as fully depleted semiconductors by assuming a uniform doping concentration and relative dielectric constant. They point out, by examining the influence of doping on relations between macroscopic and microscopic behaviors, that the uniform field approximation is inaccurate for interpreting ferroelectric semiconductor thin film behavior. Chai *et al.*[11,12] improved the physical description of MFM structures by considering a spatially varying permittivity inside the film.

It must be noticed that for all of these studies,[10–12] the polarization is always split into a linear and a switching component. As a consequence, for the relative dielectric constant ϵ_r which is the coefficient of the linear contribution, two cases have been examined. (1) ϵ_r is directly assumed to have

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an abrupt or gradual depth dependence for the relative dielectric constant; the profile is defined at the beginning of the simulation and kept constant, thus it does not depend on external bias (2) ϵ_r depends on the external bias by mean of an abrupt or gradual electric field dependence defined at the beginning of the simulation. As a consequence, a nonuniform electric field induces a spatially varying permittivity. A similar approach has been used by Kimm and Lee[13] to study the effect of the space charge distribution on the hysteresis loop properties.

In these studies, the relative dielectric constant is independent of the polarization state. In the present article we propose a model in which such assumptions are not made.

By choosing a thermodynamical approach based on the Landau–Devonshire theory,[14] the polarization is not split into two terms. That allows us to write Poisson's equation for a ferroelectric semiconductor, accounting for a differential permittivity which is polarization and electric field dependent. In these conditions, hypotheses on the permittivity depth dependence are not required because it is derived from the other parameters. It seems to us that by the use of this approach, spatial dependence of the permittivity is less artificially taken into account.

Since the presence of charges in the ferroelectric semiconductor is accounted for, a spatial variation of the electric field and thus effects on the hysteresis loops are expected. We report results obtained by assuming a uniform space charge distribution inside the film.

This article is organized as follows: In Sec. II, we describe the physical foundations of this study. The major features of the model are presented in Sec. III. In Sec. IV we investigate the influence of the bulk correlation length and the doping level on ferroelectric properties. The main conclusions are summarized and discussed in Sec. V.

II. THEORITICAL BACKGROUND

In this article we focus on the properties of a ferroelectric capacitor, we have considered the classical structure of a MFM sandwich, and have studied its response to an external bias V_{ext}.

The direction of the polarization is assumed to be perpendicular to the film surface. We thought that the original idea proposed by Ishibashi,[15] which consists of both modeling ferroelectric by a lattice model and using a thermodynamical approach, is suitable for thin film description when the surface effect is accounted for. In this section we describe the basis foundations of the model.

The phenomenological Landau–Devonshire theory which describes the properties of ferroelectric phase transitions, can also be employed to describe the thermodynamic stability of a ferroelectric in a bistable polarized configuration and to predict the response of a dipole to an applied electric field.[14,16–18] In this context, one of the simplest models is the so-called p^4 model for which the thermodynamic potential of one dipole is written as

$$V_{p^4}(p) = \frac{\alpha}{2}p^2 + \frac{\beta}{4}p^4, \tag{1}$$

with $\alpha = a(T - T_c)$, $a > 0$ and $\beta > 0$, where T is temperature and T_c the Curie temperature.

When the electric field e is applied to the dipole, its free energy F becomes

$$F = V_{p^4}(p) - pe. \tag{2}$$

A dipole which manifests the properties of hysteresis [i.e., spontaneous polarization ($p_s = \sqrt{-\alpha/\beta}$) and coercive field ($e_c = -2\alpha/3\sqrt{3}\sqrt{-\alpha/\beta}$] is described in Laudau's theory with a simple bistable system characterized by two parameters α and β. This kind of loop is often called an ideal hysteresis loop because of the abrupt transition at e_c.

Based on the continuum mean-field theory, a form of free energy for ferroelectric thin films has been developed and a so-called "extrapolation length" λ, which measures the strength of coupling in the surface layer,[19,20] was introduced to describe the change of the local polarization near a free surface of a ferroelectric. Since we have chosen to describe a ferroelectric by an ensemble of dipoles, it is necessary to include the effects of interactions between them in the free energy expansion. We use the following formula to determine the free energy of a bulk material F_V:

$$F_V = \int_V f[P(\mathbf{r})]d\mathbf{r}, \tag{3}$$

with

$$f[P(\mathbf{r})] = V_{p^4}[P(\mathbf{r})] + \frac{\kappa}{2}[\nabla P(\mathbf{r})]^2 - \int_0^P E[P'(\mathbf{r})]dP'(\mathbf{r}), \tag{4}$$

where κ is the interaction coefficient between dipoles.

Physically, the second term of Eq. (4) corresponds to the polarization gradient between neighboring dipoles and essentially provides an energy penalty for the formation of such gradient.

The film free energy is obtained by adding a surface term which depends on κ and λ so that it is given by

$$F_{\text{film}} = F_V + F_{\text{surface}}, \tag{5}$$

with

$$F_{\text{surface}} = \int_S \frac{\kappa}{2\lambda}[P^2(x,y,z=0^+) + P^2(x,y,z=L^-)]dxdy. \tag{6}$$

It can be noticed that F_{surface} includes boundary conditions at the surfaces

$$\left.\frac{dP}{dz}\right|_{z=0} = \frac{P(0^+)}{\lambda} \text{ and } \left.\frac{dP}{dz}\right|_{z=L} = \frac{P(L^-)}{\lambda}. \tag{7}$$

One of the key points in determining the equilibrium configuration $P(\mathbf{r})$ by applying the variational principal ($\delta F_{\text{film}}/\delta P = 0$) is the mathematical expression of the electric field $E[P'(\mathbf{r})]$.

The electric displacement **D** is related to the electric field **E** and the polarization **P** by the following equation:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}, \tag{8}$$

where ϵ_0 is the permittivity of free space.

Maxwell's first equation establishes a relation between the electric displacement **D** and the charge density ρ

$$\nabla \mathbf{D} = \rho. \tag{9}$$

If we consider the simple case of a one-dimensional ferroelectric capacitor $\mathbf{P}=P\mathbf{z}$, by assuming a linear relation between polarization and electric field $P=\varepsilon_0 \chi E$, we obtain Poisson's equation

$$\frac{\partial E}{\partial z} = \frac{\rho(z)}{\epsilon_0 \epsilon_r}, \tag{10}$$

where ϵ_r is the relative dielectric constant defined as

$$\epsilon_r \equiv 1 + \chi = 1 + \frac{1}{\epsilon_0}\frac{P}{E}. \tag{11}$$

Equations (10) and (11) are valid for a dielectric material. If we now assume the following classical relation $P = \epsilon_0 \chi E + P_s$, in which the polarization is split into a linear component $\epsilon_0 \chi E$ and a switching component P_s. Equations (10) and (11) stay valid only if we assume that P_s is uniform inside the film (i.e., the contribution of the surface effects is neglected). Notice that splitting P_s implies considering another approach than the thermodynamical one adopted by us. For example, Chai *et al.*[10–12] uses a hyperbolic tangent function to describe the relation between the electric field and the polarization.

Without any assumptions on the polarization-field dependence, Maxwell's first equation leads to the following equation:

$$\frac{\partial E}{\partial z} = \frac{\rho(z)}{\epsilon_0 + (\partial P/\partial E)}, \tag{12}$$

a differential permittivity can be defined as

$$\varepsilon \equiv 1 + \frac{1}{\epsilon_0}\frac{\partial P}{\partial E}, \tag{13}$$

and Poisson's equation for a ferroelectric takes the same appearance as for a dielectric

$$\frac{\partial E}{\partial z} = \frac{\rho(z)}{\epsilon_0 \varepsilon(E,P)}. \tag{14}$$

The electric field position dependence given by Eqs. (10) and (14) are quite different. Let us examine the case where $\rho(z)=0$, Eqs. (10) and (14) both lead to a uniform electric field. On the contrary when $\rho(z)\neq 0$ these equations are expected to lead to different results.

In the present work we have adopted Eq. (14) which seems to us more consistent and interesting due to the model foundations.

It can be noticed that in these conditions ε is an intrinsic model parameter and that the effect of the spatial variation of the polarization is not included by means of a bound charge density inside the numerator of the right part of Eq. (14) but by a differential permittivity inside the denominator of the right part of this equation. An increase in the differential permittivity tends to reduce the slope of the electric field inside the ferroelectric.

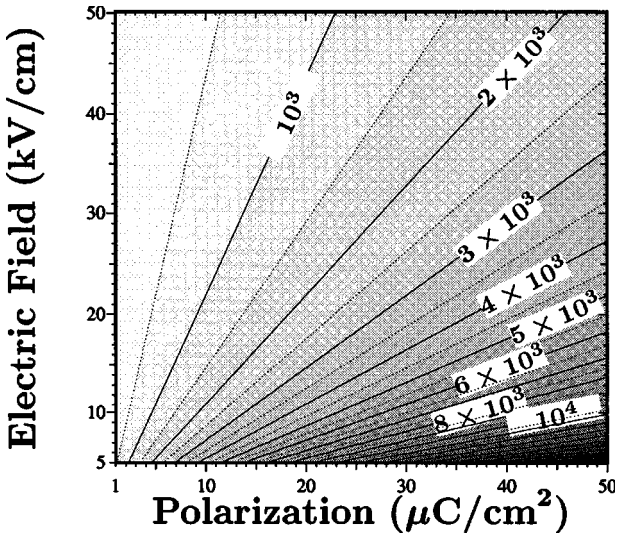

FIG. 1. Zero field differential permittivity for a dipole as a function of e_c and p_s.

The fact that for a ferroelectric, the polarization-field dependence is not simple and that the second member of Eq. (14) depends on the polarization states makes the determination of the internal electric field more difficult than for a classical dielectric. In these conditions a numerical approach is generally required, while for a dielectric one an analytical one is often possible, obviously according to the charge distribution $\rho(z)$ and neglecting the surface effect. This reason can explain why, despite the strong assumptions listed, the choice of Eq. (10) for determining the electric field in a ferroelectric material is often made.

III. DIPOLE PROPERTIES AND MODEL DESCRIPTION

It is interesting before studying thin film (i.e., the lattice), to examine the properties of a dipole.

The permittivity is defined as $\varepsilon(e,p) = 1 + (1/\epsilon_0)\,(\partial p/\partial e)|_{(e,p)}$ although it strongly depends on the polarization state (e,p) and thus on the parameters e_c and p_s which define the polarization-field relation.

We have investigated the dependence of the zero field differential permittivity $\varepsilon(e=0)$ with the parameters e_c and p_s. Figure 1 shows that according to the value of e_c and p_s, $\varepsilon(e=0)$ can drastically change. For example, the zero field permittivity of a dipole which corresponds to the hysteresis parameters often reported for PZT thin films ($e_c = 35$ kV/cm and $p_s = 30\ \mu$C/cm^2) is about 2000. More often ϵ_r is determined by using the classical formula $\epsilon_r = CL/\epsilon_0 A$, where C is the capacitance measured and A the area of the capacitor. The ϵ_r values usually obtained for PZT are about 600–800. The discrepancy between the values of ε and ϵ_r which correspond to the same value of the coercive field and remanent polarization clearly indicates that e_c and p_s must be considered as model parameters.

We have chosen to describe the ferroelectric by an ensemble of 200×200 dipoles uniformly distributed in a square lattice and characterized by the same Landau–Devonshire polynomial of Eq. (1). For the dipole parameters, we have taken $p_s=30\ \mu\mathrm{C/cm^2}$ and $e_c=35\ \mathrm{kV/cm}$. The polarization of the dipole located at i,j is $p_{ij}\mathbf{z}$, each dipole lying in the double V_{p^4} potential and interacts with its first neighbors.

The polarization is a function of the electric field, which itself is a function of time due to the variation of external bias V_{ext} and polarization state. The dynamic behavior is characterized by a viscocity coefficient γ which causes the delay in individual dipole switching.[21,22] The polarization response of the dipole i,j to the local electric field e_{ij} is determined using the following equation.

$$p_{ij}(t+\Delta t)=p_{ij}(t)-\frac{\Delta t}{\gamma}\left\{\alpha p_{ij}(t)+\beta[p_{ij}(t)]^3-\frac{\kappa_1}{h^2}[p_{i+1j}(t)+p_{i-1j}(t)-2p_{ij}(t)]-\frac{\kappa_2}{h^2}[p_{ij+1}(t)+p_{ij-1}(t)-2p_{ij}(t)]-\frac{\kappa_3}{2h^2}[p_{i+1j+1}(t)+p_{i+1j-1}(t)+p_{i-1j+1}(t)+p_{i-1j-1}(t)-4p_{ij}(t)]-e_{ij}(t)\right\}, \tag{15}$$

where h is the lattice parameter, κ_1, κ_2, and κ_3 are the interaction coefficients between first neighboring dipole. The coefficient γ has been arbitrarily set to 0.625 V ms/C for our calculations.

The polarization of the film P is determined averaging the local polarization p_{ij} over the number of dipole, and the electric field e_{ij} is derived from the electrostiatc potential v_{ij}

$$e_{ij}=-\nabla v_{ij}, \tag{16}$$

which is itself obtained solving two-dimensional Laplace's equation, using the finite differences method

$$v_{ij}=\frac{\rho_{ij}h^2}{4\epsilon_0\varepsilon_{ij}}+\frac{v_{i-1j}+v_{i+1j}+v_{ij+1}+v_{ij-1}}{4}. \tag{17}$$

Since the polarization p_{ij} of the dipole located at i,j and the electric field e_{ij} are known, the value of $\varepsilon_{ij}=1+(1/\epsilon_0)\,(\partial p_{ij}/\partial e_{ij})|_{(e_{ij},p_{ij})}$ can be determined by the use of the following method. Due to its definition, it is clear that ε characterizes the capability for the polarization to be switched under an applied field.

In order to determine the term $\partial p_{ij}/\partial e_{ij}$, we apply to the dipole ij, a virtual field Δe, and calculate a virtual polarization $p(e_{ij}+\Delta e)$ so that

$$\left.\frac{\partial p_{ij}}{\partial e_{ij}}\right|_{(e_{ij},p_{ij})}=\lim_{\Delta e\to0}\frac{p_{ij}(e_{ij}+\Delta e)-p_{ij}(e_{ij})}{\Delta e}. \tag{18}$$

When ε_{ij} is known, Eqs. (15) and (17) are solved (i.e., v_{ij}, e_{ij}, and p_{ij} are determined). We have pointed out the interdependence of ε_{ij}, v_{ij}, e_{ij}, and p_{ij} at each time. As a consequence, Eqs. (15) and (17) are solved self-consistently until the determination of these parameters with an accurate precision is achieved.

Equations (15) and (17) are related to dipoles inside the lattice. For dipoles located on the side perpendicular to the electrode, we have taken cyclic boundary conditions $p_{n+1,j}=p_{1,j}$, $p_{0,j}=p_{n,j}$, $v_{n+1,j}=v_{1,j}$, and $v_{0,j}=v_{n,j}$.

The polarization at the electrode side is given by Eq. (7) and the effect of the external bias is introduced by taking $v_{i,0}=0$, $v_{i,n}=V_{\mathrm{ext}}$ on the electrode side. In the present article, we show and discuss results concerning the polarization-field response at low frequency (100 Hz), the loops and profiles across the film correspond to a steady state for all the model parameters.

IV. RESULTS

PZT bulk materials are generally described as a p-type semiconductor while PZT thin films exhibit n-type semiconductor properties.[23] The sign of the space charges and carriers is a crucial point to describe charges injection and conduction phenomena. Since the present study is devoted to the hysteresis properties, the sign of the space charge is not a point of fundamental importance. Indeed the hysteresis loops only depend on the absolute value of the space charge density. For this reason and also in order to compare our results with some previously published,[10,13,18] we have presented in this article results obtained by considerering PZT as a p-type semiconductor. Obviously, we have verified that the sign of the space charges only affect the profiles of potential, electric field, polarization, and permittivity. The profiles for n-type ferroelectric semiconductors can easily be deduced by invoking symmetrical considerations. Another key point is the space charge distribution. Is it located close to the surface or is it occupied on all the film? For example, the fatigue phenomena is often explained by the extent of the space charge width from a region located close to the electrode toward the middle of the film. For the present study we have assumed that the space charge layer width corresponds to film thickness and that it is not modified by the external bias. In these conditions the comparison with previous modeling results is possible.[10,13,18] Moreover, we have verified that the fully depleted assumption was verified for each case studied in the present article by using the method described in the annex of Chai's article.

We have considered a 0.3-μm-thick film which is assumed to be fully depleted with a uniform space charge density N of negative elementary charges ($q=-1.6\times10^{-19}$ C) so that the charge density $\rho(z)$ and ρ_{ij}, which appear respectively in Eqs. (14) and (17), are taken equal to qN. The extrapolation length has been set to 10^{-9} m.

We have used the two-dimensional (2D) lattice model described in the previous subsection. Because of the boundary conditions along the z axis, the physical quantities of interest only depend on the depth in the film, thus profiles (1D graphs) are suitable for the results analysis. That point, which has also been discusssed in Ref. 24, is more related to the code development and further investigation than to the present physical problem studied.

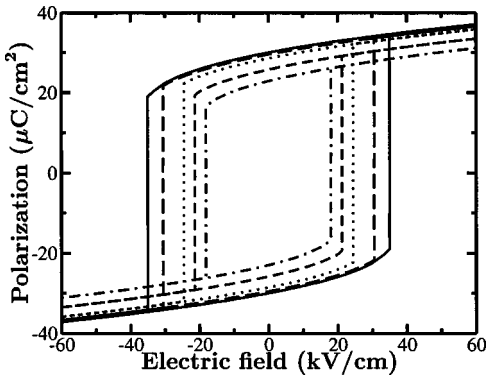

FIG. 2. Hysteresis loops for a 0.3-μm-thick film. The solid line corresponds to the case where no surface effect is included. Other calculations have been made by taking $N=5\times10^{15}$ cm^{-3} and including the surface effect. Several values of ξ have been considered. $\xi=10^{-9}$ m (long dashed line), $\xi=5\times10^{-9}$ m (dotted line), $\xi=15\times10^{-9}$ m (dashed line), and $\xi=25\times10^{-9}$ m (dashed-dotted line).

Poisson's equation [Eq. (14)] implies that a permittivity which is field dependent can have a profound effect on the magnitude of the internal field. In the following subsections we will discuss the interdependence of the permittivity and the electric field for a ferroelectric semiconductor thin film. Inside the film the electric field and the polarization are strongly position dependent. The permittivity is polarization and electric field dependent, thus we have studied the permittity behavior inside the film which is always a question of interest.

We have focused on the influence of two parameters on the ferroelectric properties: the correlation length $\xi=\sqrt{\kappa/|\alpha|}$ and the space charge density N.

A. Influence of ξ

We have studied the influence of the correlation length ξ on the polarization-field dependence. By using a thick solid line, we have plotted in Fig. 2 the loop obtained when the surface effect and the space charge field are both neglected. In this case, the electric field inside the film is equal to the external field and the polarization is uniform. The film exhibits the ferroelectric properties of a dipole ($P_r=p_s=30$ μC/cm^2 and $E_c=e_c=35$ kV/cm). We have also plotted in Fig. 2 the hysteresis loops obtained when surface effects and space charge density were both included. The space charge density was taken equal to 5×10^{15} cm^{-3} and several values of ξ have been considered. As shown in Fig. 2, when the correlation length increases the loops become more and more constricted.

We explain that behavior by using the profiles of potential (a), electric field (b), polarization (c), and permittivity (d) obtained at P_r^+ (Fig. 3). When the correlation length increases, the reduction of the polarization in the interior of the film is enhanced [Fig. 3(c)] because of the augmentation of coupling between dipoles. We have described in detail this phenomena in one of our previous studies.[24] As shown in Fig. 3(c), the polarization profiles at P_r^+ become less and less symmetrical when ξ increases. In our previous work the polarization profiles were always symmetrical so that we have tried to find an explanation of this behavior.

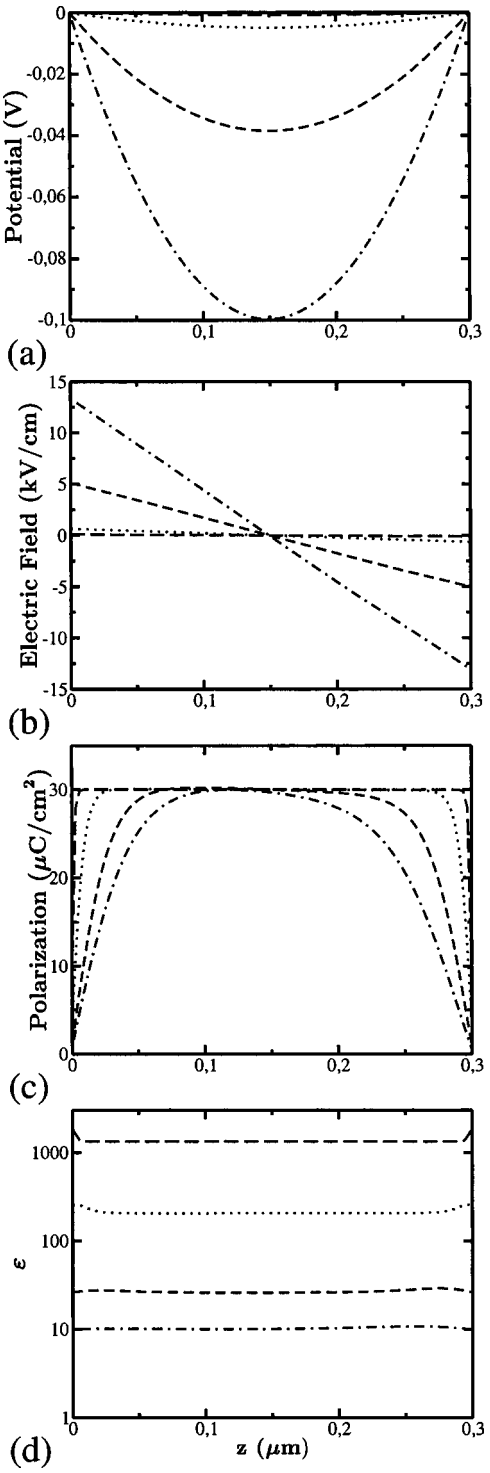

FIG. 3. The profiles of potential (a), electric field (b), polarization (c), and differential permittivity (d) inside an 0.3-μm-thick film are presented. Calculations have been made by taking $N=5\times10^{15}$ cm^{-3}. Several values of ξ have been considered. $\xi=10^{-9}$ m (long dashed line), $\xi=5\times10^{-9}$ m (dotted line), $\xi=15\times10^{-9}$ m (dashed line), and $\xi=25\times10^{-9}$ m (dashed-dotted line).

Due to the mathematical expression for Poisson's equation [Eq. (14)], the effect induced by the polarization variations inside the film is accounted for by means of the differential permittivity. This description is quite different from that generally encountered in which the bound charges produce an electric field $E_{bc}=\int-\mathrm{div}\,P/\epsilon_0\,dz$.[24] In that study, we have considered the ferroelectric as an insulator $\rho=0$: The

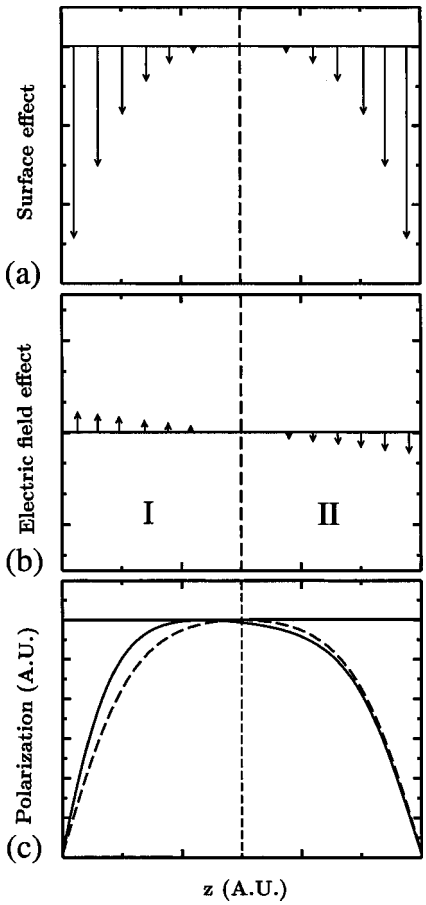

FIG. 4. Sketch of the surface effect (a) and space charge field effect (b) for low space charge density. Arrows have been used to show the direction and the magnitude of these effects on the polarization. The resulting polarization profiles (c) are shown for two cases: (1) neglecting the contribution of the space charge field (b) so that only the surface effect (a) is accounted for (dashed line), (2) accounting for the contribution of the surface effect (a) and of the space charge field (b) (solid line).

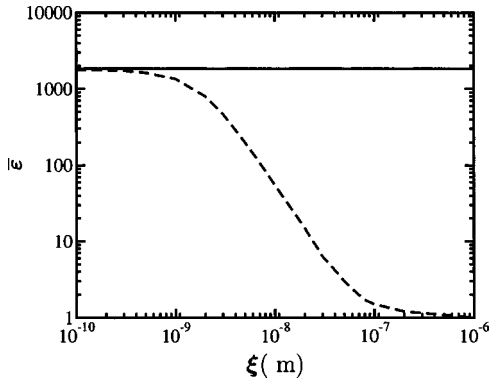

FIG. 5. The permittivity mean value $\bar{\varepsilon}$ is plotted as a function of the correlation length ξ. The horizontal line corresponds to the dipole value (noninteracting medium).

electric field has two components $E=E_{ext}+E_{bc}$ where $E_{ext}=V_{ext}/L$ is the external field. For a ferroelectric semiconductor we would have $E=E_{ext}+E_{bc}+E_{sc}$ with $E_{sc}=\int \rho/\epsilon_0\, dz$. A study accounting for this approach will be reported in a future article. It is clear that for the present study the electric field has only two components, the external one E_{ext} and the space charge one $E_{sc}=\int \rho/\epsilon_0 \varepsilon(E,P)\, dz$. The discussion of the results must be limited invoking these two field effects and the surface effect.

At remanent state P_r^+ the external field is null only the effect of the space charge field component is observed in Fig. 3. It must be noted that the potential profiles exhibit a parabolic shape [Fig. 3(a)], the electric field profiles are linear,[25] and exhibit two regions of opposite field directions [Fig. 3(b)]. We now focus on the explanation of the phenomena observed in Fig. 3(c): As the correlation length gets higher, the polarization profile becomes more and more asymmetrical. In order to illustrate the discussion, the effect of the surface effect (a) and space charge field effect (b) are sketched separately in Fig. 4.

Since the surface effect is accounted for by the same boundary conditions for each side, the polarization decreases with the same magnitude in the vicinity of each side [Fig. 4(a)]. The effect produced by the space charge field is described in Fig. 4(b). On the left side of this figure, the electric field is positive, as is also the polarization. Thus the field effect is polarizing and opposite to the surface effect. As a consequence in this region of the film, the magnitude of the polarization decrease is reduced by the space charge field effect. On the right side, the electric field is negative, the effects are both depolarizing. Thus on this side, the magnitude of the polarization decrease is enhanced by the space charge field. As a consequence the polarization profile is asymmetrical [Fig. 4(c)].

The hysteresis loop obtained for the lowest values of the correlation length $\xi=10^{-9}$ m is, as shown in Fig. 2, very close to the dipole one. The band bending of the potential is very weak and the electric field close to zero [Figs. 3(a) and 3(b)]. This point is easily explained by the weak surface effect inside the film observed in Fig. 3(c) so that the electric field inside the film is almost reduced to the external component which is null in the short circuit conditions. The surface effect increases with ξ the potential band bending and the electric field are then enhanced.

We observe, despite the low space charge densities that the electric field close to the surface is not weak. That may appear to be strange. Nevertheless, by examining the permittivity profiles, we can explain the discrepancy between both the values. As shown in Fig. 3(d),[26] ε exhibits a strong ξ dependence. We observe that when ξ increases, the permittivity strongly decreases. As a consequence, despite the low space charge density $N=5\times10^{15}$ cm^{-3}, the effect produced by the space charge on the electric field values is important for the highest values of ξ because of the low ε value.

We have plotted in Fig. 5 the evolution of the mean permittivity $\bar{\varepsilon}=1/L\int_0^L \varepsilon(z)dz$ as a function of ξ. When ξ goes to zero, which corresponds to the case of a noninteracting medium, we found again the zero field dipole permittivity for the $\bar{\varepsilon}$ value. When ξ increases, we observe that $\bar{\varepsilon}$ decreases, and reaches 1 for infinite ξ. This corresponds to $\partial p/\partial e=0$ which means that it is impossible to switch the polarization. It is necessary to remember that ε is a local parameter when explaning the evolution of ε with ξ. As a consequence a local variation of δp induced by a local variation δe produces an increases of free energy through the gradient term which increases as ξ gets higher. As a consequence the variation of

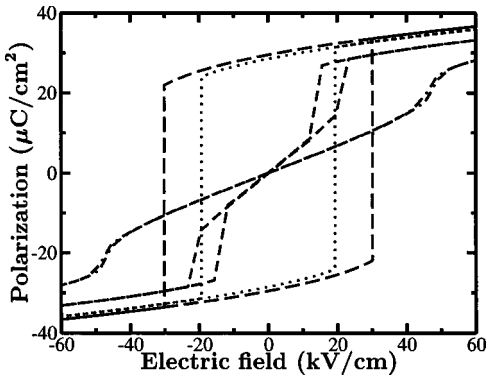

FIG. 6. Hysteresis loops for a 0.3-μm-thick film. Calculations have been made by taking $N=5\times10^{16}$ cm^{-3} and including the surface effect. Several values of ξ have been considered. $\xi=10^{-9}$ m (long dashed line), $\xi=5\times10^{-9}$ m (dotted line), $\xi=15\times10^{-9}$ m (dashed line), and $\xi=25\times10^{-9}$ m (dashed-dotted line).

the polarization corresponds to a less favorable situation as the correlation increases. In other words ε decreases due to the energy minimization.

Then we have studied the ferroelectric properties for a ten times higher space charge density. The polarization-field dependencies are plotted in Fig. 6. It appears, as compared to Fig. 2, that the degradation of the ferroelectric properties is more pronounced. The potential band bending [Fig. 7(a)] is more important and the slope of the electric field [Fig. 7(b)] is almost ten times higher than that shown in Fig. 3(b).

As a consequence, for a given value of ξ the effect of the space charge field on the polarization profiles is more important [Fig. 7(c)]. An opposite polarization structure then appears for the highest values of ξ considered.

In order to explain this phenomena, we have sketched in Fig. 8 the effect of the surface effect (a), the effect of the electric field (b), and the influence on the polarization (c). Due to the ten times higher space charge density, the electric field exceeds the coercive field values $-e_c$ close to the surface [Fig. 8(b)]. As a consequence the polarization switching occurs in this region [Fig. 8(b)].

Despite the field value $-e_c$ is not reached everywhere in this half side of the film and polarization reversal occurs elsewhere in this half side because of the free energy minimization. That leads to the formation of an opposite polarization region structure.

It must be noted that contrary to what we have observed for a ten times lower space charge density, [Fig. 3(c)] the effect of the boundary conditions does not extend in the depth of the film [Fig. 7(c)]. In fact it is located in the close vicinity of the surface and is responsible for the decreases of $|P|$ on each side.

We have found that the space charge density values for which ferroelectric properties were strongly affected by the space charge field was about two orders of magnitude lower than these predicted by nonthermodynamical modeling approaches.[10,13] In order to explain that phenomena, it is necessary to note that usually the permittivity ϵ_r, which is used in these models, is determined from experimental data by calculating the slope of the hysteresis loop at the remanent state or by using the capacitance measurements. In these conditions it is clear that the permittivity is a nonlocal parameter because that is the variation of the mean polarization over thickness of the film which is measured. For modeling approaches cited therein, the polarization everywhere is fully determined by the knowledge of the alone electric field calculated from the ideal dielectric Poisson's equation in which ϵ_r is introduced [Eq. (10)]. Moreover, because transient

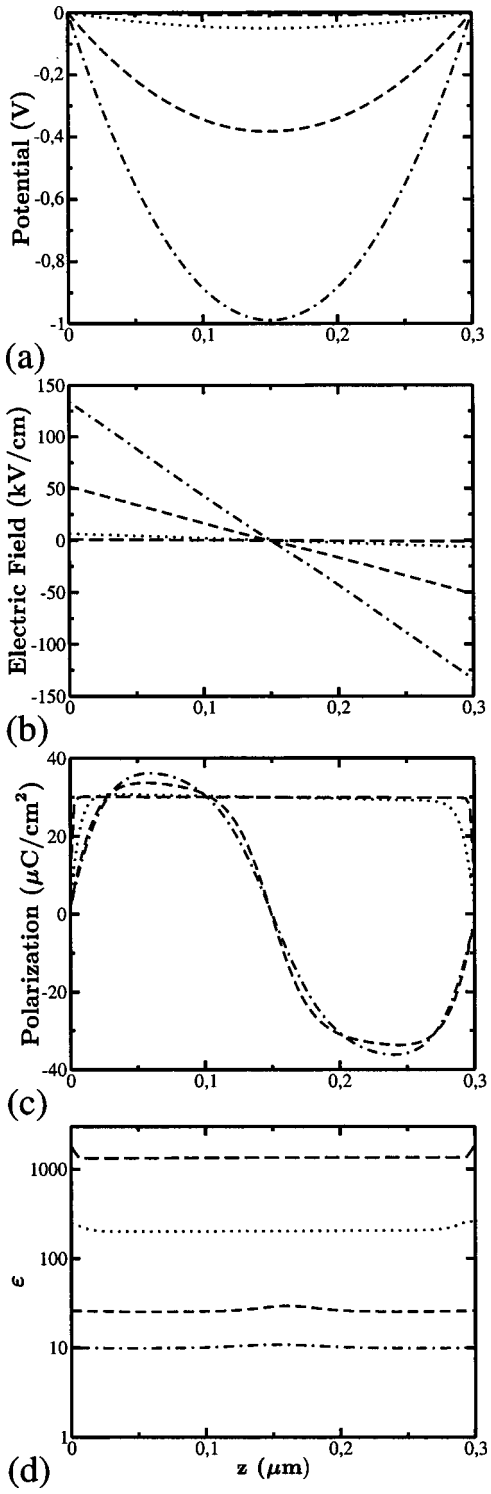

FIG. 7. The profiles of potential (a), electric field (b), polarization (c), and differential permittivity (d) inside a 0.3-μm-thick film are presented. Calculations have been made by taking $N=5\times10^{16}$ cm^{-3}. Several values of ξ have been considered. $\xi=10^{-9}$ m (long dashed line), $\xi=15\times10^{-9}$ m (dotted line), $\xi=15\times10^{-9}$ m (dashed line), and $\xi=25\times10^{-9}$ m (dashed-dotted line).

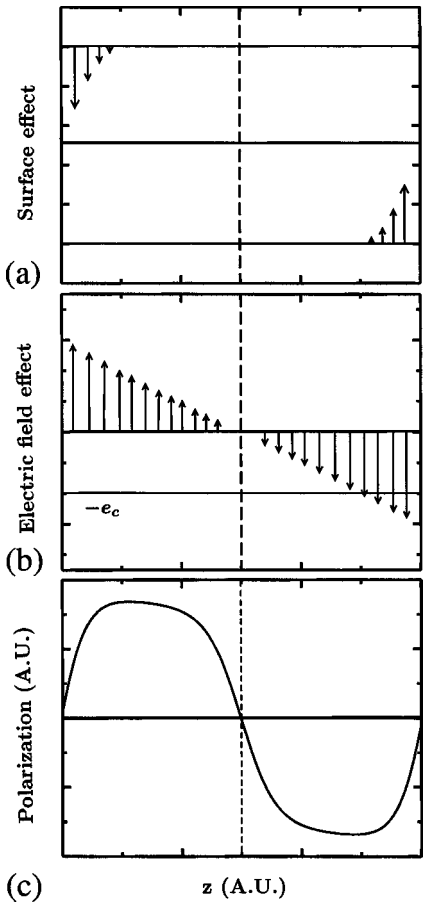

FIG. 8. Sketch of the surface effect (a) and space charge field effect (b) for high space charge density. Arrows have been used to show the direction and the magnitude of these effects on the polarization. The resulting polarization profile (c) in which both effects are seen to be effective.

states are not described that also implicitly means that the local polarization variations are instantaneous. In other words, despite the interest that such kinds of modeling approaches have, we cannot fully trust these descriptions for thin film properties because what happens inside the film between two steady states is not described. Obviously what happens after the initial state determines the final state. As previously discussed,[27] the physical basis of our model is well adapted to the classical description of ferroelectricity, a collective phenomena (because of the thermodynamical description), an inhomogeous switching (because of the evolution equation). Moreover for the present study, the local variation of the polarization is influenced by the local electric field determined by using the local parameter ε and the contribution of the free energy gradient. For us, these remarks could explain the discrepancy of space charge density range of values necessary to make ferroelectric properties vanish in both kinds of approaches.

The next section is devoted to a detailed explanation of the influence of this parameter.

B. Influence of *N*

In this section, we will study the influence of the space charge density N on the ferroelectric properties. We have

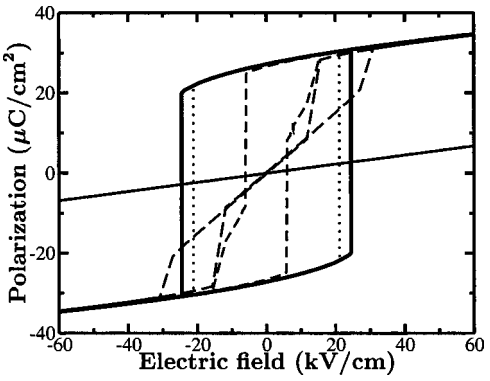

FIG. 9. Hysteresis loops for a 0.3-μm-thick film. Calculations have been made, including the surface effect and by taking $\xi=10^{-8}$ m. Several values of N have been considered. $N=10^{15}$ cm^{-3} (thick solid line), $N=10^{16}$ cm^{-3} (dotted line), $N=5\times10^{16}$ cm^{-3} (dashed line), $N=10^{17}$ cm^{-3} (long dashed line), and $N=10^{18}$ cm^{-3} (solid line).

plotted in Fig. 9 the polarization-electric field dependencies obtained for several values of the space charge density.

The loop which corresponds to the lowest space charge density studied ($N=10^{15}$ cm^{-3}) is very close to these obtained for a ferroelectric insulator ($N=0$) (only one of them has been presented in Fig. 9). Let us remark that this loop is constricted with respect to the dipole one ($P_r<p_s$ and $E_c<e_c$). Because the results for $N=0$ and $N=10^{15}$ cm^{-3} are very close, that means for $N=10^{15}$ cm^{-3}, the contribution of the space charge field to the ferroelectric properties is negligible. In other words the constriction of the loop observed for $N=10^{15}$ cm^{-3} is only due to the surface effect. A more detailed study concerning the influence of N on the hysteresis parameters P_r and E_c will be reported at the end of this section.

When the space charge density increases the constriction of the hysteresis enhances and successively a double loop hysteresis and a linear behavior are observed.

For a better understanding of these phenomena, we have represented in Fig. 10 the profile for V, E, P, and ε at the remanent state P_r^+. When there is $N=10^{15}$ cm^{-3} space charge density, the space charge field is very weak. The electric field is almost reduced to the external component $E=E_{\text{ext}}$. As a consequence the electric field inside the film is uniform, null at P_r^+ [Fig. 10(b)]. The polarization is only influenced by the surface effect (Fig. 4) and thus exhibits a symmetrical profile with respect to the middle axis of the film. The polarization is reduced close to the surface and is equal to the dipole polarization in the interior of the film [Fig. 10(c)].

When $N>10^{16}$ cm^{-3} the potential exhibits a parabolic shape [Fig. 10(a)], the magnitude of the potential band bending is enhanced by the space charge density augmentation. The electric field is linear and two regions of opposite in sign electric field are observed in Fig. 10(b). As the space charge density gets higher, the slope of the electric field distribution increases and for the highest values of N, the electric field is higher than e_c on the left side and lower than $-e_c$ on the right side. As a consequence the mechanism already seen in the previous section and described in Fig. 8 leads to the formation of an opposite polarization region structure. In fact the evolution of the loop with N is very similar to those one observed with ξ.

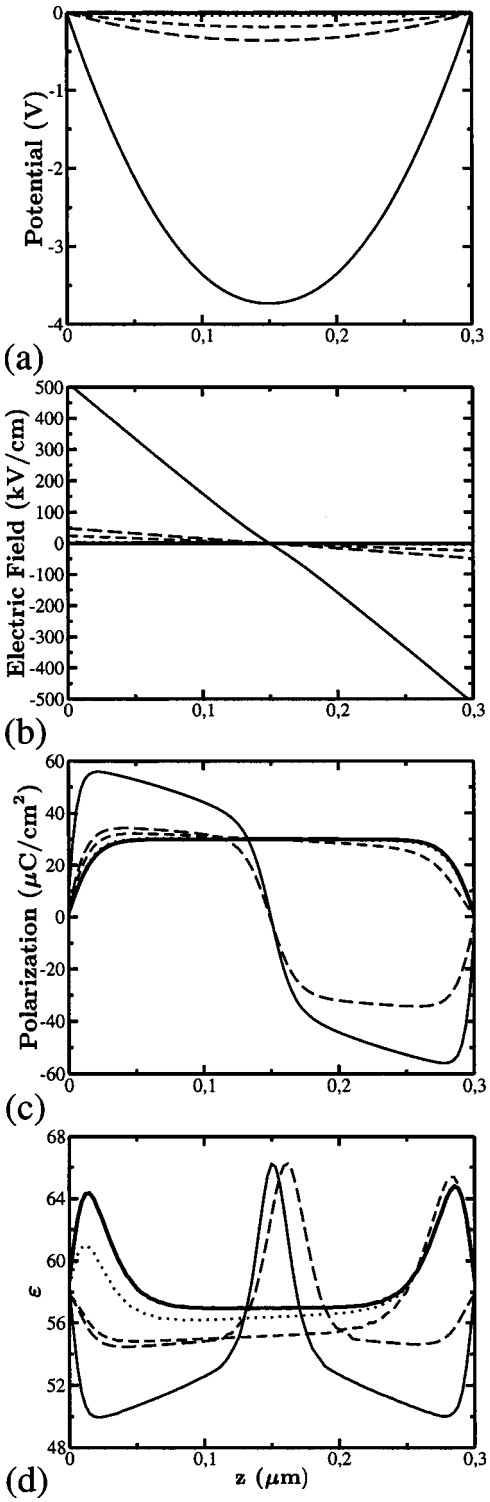

FIG. 10. The profiles of potential (a), electric field (b), polarization (c), and differential permittivity (d) inside an 0.3-μm-thick film are presented. Calculations have been made, including the surface effect and by taking $\xi = 10^{-8}$ m. Several values of N have been considered. $N=10^{15}$ cm^{-3} (thick solid line), $N=10^{16}$ cm^{-3} (dotted line), $N=5\times10^{16}$ cm^{-3} (dashed line), $N=10^{17}$ cm^{-3} (long dashed line), and $N=10^{18}$ cm^{-3} (solid line).

The distribution of the electric field inside the film at a given bias is completly determined by the knowledge of $\varepsilon(E,P)$ and N. Due to the spatial variation of the electric field and the polarization, the permittivity is expected to change through the depth of the film.

In the previous section we have focussed on the explanation of the order of magnitude of ε, which strongly depends on ξ, so that we have adopted a logarithmic scale [Fig. 3(d)] in these conditions where the polarization profile appeared to be uniform inside the film. Contrary to what we obtained in the previous section, the order of magnitude of ε is not strongly influenced by the space charge density.

We now focus on the explanation of the detail of the ε profile shape. As shown in Fig. 10(d) the ε profile strongly depends on the space charge density N. Two peaks of permittivity are observed for $N=10^{15}$ cm^{-3}, one near each side. Those kinds of profiles have also been reported for the susceptibility by Zhong *et al.*[28] and by Glinchunk *et al.*[29] for ferroelectric insulators.

For low space charge density ($N=10^{16}$ cm^{-3}), the permittivity profile is slightly more asymetrical (dotted line). The peak of permittivity observed on the left side is less high than for $N=10^{15}$ cm^{-3}. As N increases the profiles become more and more asymmetrical (dashed line) and the peak of permittivity located at the left side vanishes.

For $N=10^{17}$ cm^{-3} an opposite polarization region structure is observed [Fig. 10(c)]. A peak of permittivity is observed close to the middle of the film and two regions of low permittivity are observed on each side of the peak. As N increases the peak of permittivity becomes more and more centered with respect to the middle of the film, and for the highest space charge density considered $N=10^{18}$ cm^{-3} the permittivity profile appears to be symmetrical.

It can be noted that the changes observed in the symmetrical properties of the permittivity profile are in close relation with the changes observed on the polarization profiles. For the lowest values of N studied the surface effect prevails over the effect induced by the space charge field. Thus polarization and permittivity profiles are symmetrical with respect to the middle of the film because the surface effect has the same magnitude on each side of the film. For medium space charge density both effects influence the polarization permittivity and symmetrical properties are not observed. For the highest values of N, the space charge effect prevails over the surface effect so that the polarization and the permittivity exhibit symmetrical profiles because they are mainly influenced by the space charge field which itself exhibits symetrical profile. Except close to the surface, we have observed that ε followed the variation of $|\partial p/\partial z|$ with z. That behavior can easily be explained as follows: The more important component of $\varepsilon(z)$ is the term $1/\epsilon_0\times\partial p/\partial e$. So that the term $\kappa(\partial p/\partial z)^2$ in Eq. (4) can be rewritten approximately $\kappa K^2\varepsilon^2\epsilon_0^2$, where K is the slope of the electric field which is almost uniform.

As a consequence, the spatial variation of the permittivity is governed by the polarization gradient. In fact the augmentation of the polarization gradient increases the free energy. This corresponds to a less favorable situation and thus the polarization is easier to switch.

Because the polarization is determined by the boundary conditions [Eq. (7)], the polarization variation at the surface is not strongly influenced by the space charge field. As a consequence $|P(0)|$ and $|P(L)|$ are almost independent of N and as is also ε at the surface.

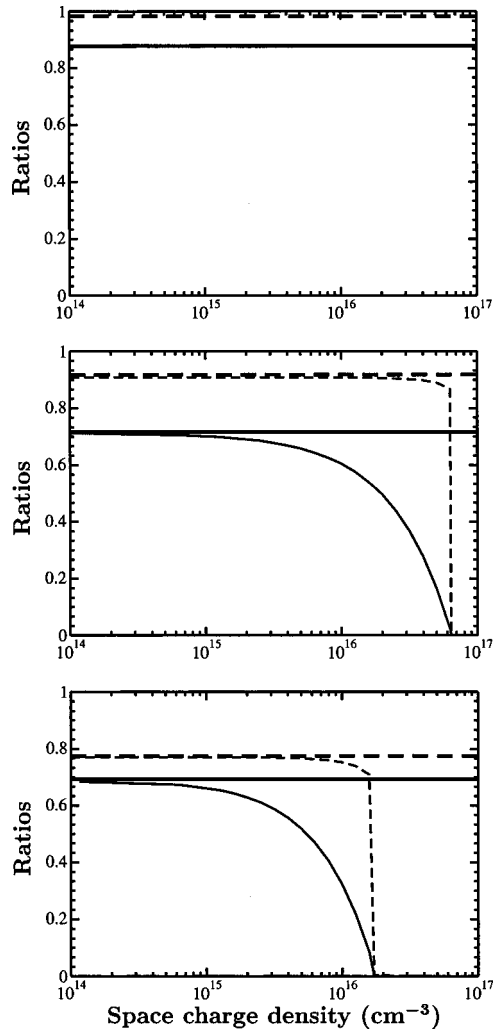

FIG. 11. The evolution of the ratios P_r/p_s (dashed lines) and E_c/e_c (solid lines) with N are presented for three correlation length values $\xi=10^{-9}$ m (a), $\xi=10^{-8}$ m (b), $\xi=2.5\times10^{-8}$ m (c). The horizontal thick lines correspond to the values obtained for a ferroelectric insulator ($N=0$). In (a) the ratio values for a ferroelectric semiconductor are identical to those obtained for the ferroelectric insulator.

These explanations are valid except in the close vicinity of the surface, i.e., near the peak locations. It is difficult to provide a simple explanation of the permittivity peaks, the permittivity behavior in the vicinity of the surface is influenced by both the boundary conditions and the polarization gradient term. These opposite effects can explain the existence of permittivity peaks because according to the position between the effect of the polarization gradient or the effect of the boundary conditions, we think that one of them prevails over the other one.

For a better understanding of the contribution of the space charge field and the surface effect toward the ferroelectric semiconductor properties, we have plotted in Fig. 11 the evolution of the ratios E_c/e_c and P_r/p_s with N for many values of the correlation length. The results are compared to those obtained for a ferroelectric insulator. For the lowest value examined $\xi=10^{-9}$ m [Fig. 11(a)], the values for the ratios are not distinguishable from those obtained for a ferroelectric insulator. The alone phenemenon responsible of the constriction of the loop ($E_c/e_c<1$, $P_r/p_s<1$) with respect to the dipole one is the surface effect. That means, in that case, that the space charge field is not sufficient to modify hysteresis properties. As expected for the highest correlation length values studied, we observe in Figs. 11(b) and 11(c) that the reduction of the ratios for a ferroelectric insulator (only due to the surface effect) increases with ξ. For a ferroelectric semiconductor the coercive field decreases with N. That clearly shows that the role of the space charge field on the switching properties is important. From about $N=6.45\times10^{16}$ cm^{-3} for $\xi=10^{-8}$ m and $N=1.72\times10^{16}$ cm^{-3} for $\xi=2.5\times10^{-8}$ m the coercive field is null, which corresponds to the appearance of the opposing region structure inside the film. It is convenient to distinguish two parts on the polarization curves [Figs. 11(b) and 11(c)]. Before the appearance of the opposing region structure, the effect of the space charge field is weak and its effect gives rise to the polarization decreases on one side and the increases on the other side (Fig. 4). Because of these opposite effects, the film polarization, which corresponds to the mean value over thickness, is close to those of a ferroelectric insulator. After the appearance of the opposing region structure, the film polarization is null because its profile is symetrical with respect to the point of zero polarization located in the middle of the film.

V. CONCLUSION

The internal description of a ferroelectric semiconductor thin film, i.e., potential, polarization, electric field, and differential permittivity variation inside the film, has allowed us to discuss their effects on the hysteresis properties.

As previously shown[24] for a ferroelectric insulator, the correlation length ξ plays an important role on the magnitude of the surface effect. In the present article we have also shown that for a ferroelectric semiconductor, the polarization profile also depends on the space charge field. The most important result is that the order of magnitude of the parameter ξ also strongly influences the permittivity ε inside the film. As a consequence, because for a ferroelectric semiconductor the parameter ε plays an important role in Poisson's equation, the space charge field is not only determined by the space charge density but also by the coupling between dipoles introduced by means of the correlation length. The permittivity ε strongly decreases when ξ increases, and as a result the electric field inside the film reaches very high values. For medium coupling, ε is very weak inside the film, and as a consquence, for low space charge density high electric fields are also observed in the ferroelectric. In other words, even without high space charge density, high space charge fields can be observed because of the low ε value induced by the coupling inside the material.

Recently, Prosandeev *et al.*,[30] by studying heterogeneous ferroelectrics, established that the susceptibility χ was conversely proportionnal to the parameter κ in front of the $(\nabla P)^2$ in Landau's equation. The Prosandeev *et al.* and present studies both show that, respectively, κ and $\xi=\sqrt{\kappa/|\alpha|}$ play an important role in the susceptibility and the permittivity values. It must be noticed that despite the differences between

the two approaches the same trend in evolution is observed: When the correlation increases, κ and $\xi=\sqrt{\kappa/|\alpha|}$ increase, as a consequence ε and χ strongly decrease.

For example, for a 0.3-μm-thick film with a space charge density $N=5\times10^{15}$ cm^{-3}, by taking $\xi=25\times10^{-9}$ m we obtained the electric field at the surface $E_{\text{surf}}=13.4$ kV/cm. That value must be compared to the value usually obtained for the case of an ideal dielectric with the same thickness when the space charge density and the polarization are uniform inside the film. The electric field at the surface can be determined by integrating Eq. (10). By taking as commonly made $\epsilon_r=300$ we obtain $E_{\text{surf}}=0.452$ kV/cm. This discrepancy between the values of E_{surf} calculated by the two methods show that very different values for macroscopic parameters inside the film can be found according to the theoretical approach employed.

A lot of works devoted to study switching[31] and conduction[32] properties or fatigue phenomenon[33] are obviously based on different physical descriptions. But they have in common that the ferroelelectric thin films are considered as partially or fully depleted and the space charge field is determined by using Poisson's equation for an ideal dielectric. In fact the crucial parameter of these approaches is the surface field E_{surf} rather than the space charge density N or the relative dielectric constant ϵ_r. The surface field produced by the space charges required to fit experimental data is, respectively, about 90, 45, and 45 kV/cm which corresponds, respectively, to different sets of parameters ($N=10^{18}$ cm^{-3}, $\epsilon_r=200$, $L=0.3$ μm), ($N=5\times10^{17}$ cm^{-3}, $\epsilon_r=300$, $L=0.3$ μm), and ($N=10^{19}$ cm^{-3}, $\epsilon_r=400$, $L=0.02$ μm). By the use of our model, the values of the surface field 90 and 45 kV/cm are, respectively, obtained for $N=3.36\times10^{16}$ cm^{-3} and $N=1.68\times10^{16}$ cm^{-3}, accounting for 25×10^{-9} m correlation length.

We have also studied the effect of the space charge density on the ferroelectric properties, and have found that the details of the ε profile shape is influenced by the value of N. Moreover, we have pointed out that the coercive field is more affected by the space charge field than the remanent polarization. It is well known that according to the space charge density the ferroelectric properties can vanish. This behavior has been reported in theoretical approaches by many authors for many years.[10–13,18] All these studies have been made by neglecting the surface effect and correlation length but accounting for the parameter ϵ_r. In fact by taking into account correlation phenomena and a permittivity, which depends on field and polarization, we have shown that the ranges of space charge density for which ferroelectric properties are modified are strongly influenced by the space charge field and could be diminished by many orders of magnitude according to the value of ξ.

The extrapolation length which plays an important role in the polarization variation close to the surface could also strongly influence the permittivity profile. Because it is well known that the magnitude of the surface effect on the ferroelectric properties increases while the thickness decreases, one can expect permittivity variations driven by size effect.

ACKNOWLEDGMENTS

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