Concerning the screening of a spontaneous-polarization field by free carriers in ferroelectrics

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A method is developed for the solution of problems involved in finding the polarization and the electric field in semiconducting ferroelectrics near boundaries or inhomogeneities. It is noted that the presence of surface states of even high density may not lead to a substantial decrease of the previously predicted band bending near the surface of a ferroelectric.

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1. INTRODUCTION

The electric field produced in a ferroelectric by its spontaneous polarization is compensated, as is well known, by breakup of the ferroelectric into domains, by surface-state charges, by adsorption of lines, etc. In those cases, however, when the concentration of the free carriers inside the ferroelectric crystal is not small, i.e., when the crystal is a semiconducting ferroelectric (SF), the screening of the spontaneous-polarization field may be effected also by these charges. It turns out that in this case a peculiar single-domain state may turn out to be energywise most favored; in this state the screening takes place in the surface region, where free carriers of the crystal accumulate.[1–6]

In theoretical investigations of problems of this kind it is customary to use the well known equation of state

$$\mathbf{E}=\delta\mathcal{F}/\delta\mathbf{D} \tag{1}$$

or its equivalents. In (1), **E**, **D**, and $\mathcal{F}$ are respectively the field, the induction, and the total free energy. It is not always convenient, however, to use Eq. (1), since this calls for knowledge of $\mathcal{F}$ at least in the equilibrium state as a functional of the induction, yet the parameters of the equilibrium state are still to be determined by solving the problem. For this reason it becomes necessary to make assumptions concerning the form of $\mathcal{F}$ as a function of **D**, for example, to assume that the density of the free energy is a polynomial of the powers and gradients of **D**.

It is clear that in the general case this assumption is not valid and the free energy of the system [more accurately, its ferroelectric part, see (2) below] is represented in the form of a series in powers of the polarization and its derivatives. Of course, in some cases, for example in cases when there is no electric field, both approaches, as is well known, are equivalent. We call attention below to a rather large class of problems in which this assumption is not valid.

One such problem, which can be used as an example to demonstrate the correct solution method, is in fact the problem of the single-domain state. The impossibility of expanding $\mathcal{F}$ in powers of the induction **D** is in this case obvious at least from the fact that the assumption usually made[1–6] that the field **E** is weak compared with the induction does not hold true near the sample boundary. In fact, solutions are possible with nonzero polarization **P** on the sample boundary, and from the boundary condition for the induction it then follows immediately that the field near the boundary need not necessarily be small (see below).

We note also that the simplifications that are possible in the case when the polarization deviates little from its equilibrium value in the volume of a bulky sample ($|\mathbf{P}-\mathbf{P}_0| \ll P_0$) cannot be used, since this inequality is violated in the case of single-domain states.

In addition to the indicated problems, we shall discuss below also the influence of surface states on the considered group of problems.

2. CASE OF SMALL BAND BENDING

We consider a uniaxial ferroelectric, in which the polarization is directed along one axis (the c axis) perpendicular to the surface of a planar sample, and we study the one-dimensional solutions for which all the functions depend only on a single coordinate z. In this case the ferroelectric part of the free energy can be written in the form[7,8]

$$F=\int\left\{f(\mathbf{P})+\frac{\varkappa}{2}\left(\frac{d\mathbf{P}}{dz}\right)^2\right\}dV, \tag{2}$$

where $f(\mathbf{P})$ is a certain polynomial of $\mathbf{P}^2$. The first term describes the self energy of the ferroelectric, which is connected with the presence of spontaneous polarization, while the second term describes the correlation energy.

Generally speaking, it is necessary to include in (2) also expressions for the dependence of F on the resultant strains. However, as shown by example by Zhirnov,[8] they lead only to a renormalization of the coefficients in (2).

We shall investigate the case when the solution for the polarization can be obtained in explicit form—the case of small band bending in a semiconducting ferroelectric: $q\varphi/kT \ll 1$, where q is the absolute value of the electron charge, k is Boltzmann's constant, and T is the temperature. We shall find it convenient to spell

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out later on the restrictions needed to realize precisely this case.

We note that although the screening by the carriers was assumed to be linear, allowance for the nonlinearity of the screening need not yield qualitatively new effects, and at the same time the linearity of the Poisson equation (3) allows us to carry the calculation through to conclusion.

Let us see how the spontaneous-polarization field becomes screened in a semi-infinite sample. We assume for the sake of argument that the vector P in the volume is directed towards the boundary, and that $0z$ axis is directed towards the interior of the semiconducting ferroelectric. Then the Poisson equation for small band bending in the SF can be written in the form

$$\varphi''=\lambda^2\varphi-4\pi dP/dz, \tag{3}$$

where $\lambda=1/R_D$ is the reciprocal of the Debye screening radius R_D with unity dielectric permeability, $-P$ is the projection of the vector P on the $0z$ axis, and φ is the potential. We assume also that there is no degeneracy in the free-carrier gas.

For an arbitrary distribution $P(z)$ we can represent the solution of (3) in the form

$$\varphi=-\int_0^\infty G(z,z_0)\cdot 4\pi\frac{dP}{dz_0}dz_0+\frac{e^{-\lambda z}}{2\lambda}\int_0^\infty \exp(-\lambda z_0)\cdot 4\pi\frac{dP}{dz_0}dz_0+4\pi P_s\frac{e^{-\lambda z}}{\lambda},$$

$$G(z,z_0)=\begin{cases}-\exp[-\lambda(z-z_0)]/2\lambda, & z>z_0\\ -\exp[\lambda(z-z_0)]/2\lambda, & z<z_0\end{cases}, \tag{4}$$

$$P_s=P(0).$$

By varying the free energy with respect to the polarization, provided that Maxwell's equations are satisfied, we easily obtain in standard fashion an equation for $P(z)$, which we can write, using (2) and (4), in the form

$$-2\pi\lambda\int_0^\infty P(z')\exp[-\lambda|z-z'|]dz'+4\pi P(z)+2\pi\lambda e^{-\lambda z}\int_0^\infty P(z')\times e^{-\lambda z'}dz'=-\frac{\partial f(P)}{\partial P}+\varkappa\frac{d^2P}{dz^2}. \tag{5}$$

We consider first (5) at large $z\gg 1/\lambda$. Then the third term in the left-hand side of (5) can be neglected, and in the right-hand term we can expand $P(z')$ in powers of $(z-z')$ and retain the first nonvanishing expression, since, as we shall presently show, at large z the polarization $P(z)$ changes substantially over distances much larger than $1/\lambda$. As a result we get the equation

$$(4\pi/\lambda^2+\varkappa)P''=\partial f/\partial P. \tag{6}$$

From (6) it follows that

$$P'=(2[f(P)-f(P_0)])^{1/2}/\rho,\quad \rho=(4\pi/\lambda^2+\varkappa)^{1/2}. \tag{7}$$

Since the quantity

$$\alpha=[f(P)-f(P_0)]/P^2$$

is usually much less than unity at all $|P|\leq P_0$ (see Refs. 1–6), we see from (7) that $P(z)$ indeed changes only over distances much larger than $1/\lambda$.

We note furthermore that Eqs. (6) and (7) are valid also at distances from the boundary much less than the characteristic lengths in (6) and (7). In fact, (6) and (7) are valid up to distances such that the third expression in (5) is small, i.e., up to z_0 for which

$$\exp(-\lambda z_0)\sim\alpha/2\pi. \tag{8}$$

From (8), recognizing that $\alpha\ll 1$, we get

$$-\frac{1}{\lambda}\ln\frac{\alpha}{2\pi}<\frac{\rho}{\alpha^{1/2}}.$$

It follows hence that

$$z_0<\rho/\alpha^{1/2}.$$

Thus, at $z>z_0$, according to (7) and (8), the polarization $P(z)$ is described by the following relation:

$$\int^P\frac{dP'}{(2[f(P')-f(P_0)])^{1/2}}=\rho z+\text{const}. \tag{9}$$

In particular, as z

$$-P+P_0=C\exp(-\alpha_0^{1/2}\rho z), \tag{10}$$

where

$$\alpha_0=\partial^2 f/\partial P^2|_{P=P_0},$$

i.e., we have pure Debye screening.

On the other hand if in some region of the values of P the function $f(P)$ has linear sections

$$f(P)-f(P_0)=A+\alpha_1P_0(P-P_1),$$
$$A=f(P_1)-f(P_0),\quad \alpha_1P_0=\partial f(P)/\partial P|_{P=P_1},$$

then in this region $P(z)$ is given, in accordance with (9), by the expression

$$P=P_1+\left\{1-\left[1-\frac{\alpha_1P_0}{(2A)^{1/2}}\rho(z-z_1)\right]^2\right\}A\frac{1}{\alpha_1P_0}. \tag{11}$$

We must determine the constants in (9)–(11). They can be obtained by matching the already obtained solutions in the region $z>z_0$ to the solution in the region $z<z_0$ at $z\sim z_0$ [see (8)]. It is necessary here to use a boundary condition that follows from the requirements that the total free energy be a minimum:

$$\partial P/\partial z|_{z=0}=0. \tag{12}$$

As we shall see below, the solution in the region $z<z_0$ depends essentially on the value of the parameter $\varkappa\lambda^2/4\pi$. We consider first the case

$$\varkappa\lambda^2/4\pi\ll 1, \tag{13}$$

when the spatial change of the polarization near the boundary is determined by the correlation length and not be screening by the free carriers. We investigate Eq. (5) in the region $z\ll 1/\lambda$, where it can be conveniently written in a form equivalent to (5):

$$P=\int_0^\infty G_1(z-z')D_1(z')dz'+Be^{-z/r}, \tag{14}$$

where

$$r=\left(\frac{\varkappa}{4\pi}\right)^{1/2},\quad G_1(z-z')=-\exp\left(-\frac{|z-z'|}{r}\right)\frac{r}{2\varkappa},$$

$$D_1(z)=-2\pi\lambda\int_0^\infty\exp(-\lambda|z-z'|)P(z')dz'+2\pi\lambda\int_0^\infty\exp(-\lambda[z+z'])P(z')dz'+\frac{\partial f(P)}{\partial P}$$

and G_1 satisfies the equation

$$\varkappa G_1''(z-z')=\delta(z-z').$$

It follows from (12) that

$$B\approx{}^1/_2 r\lambda P_\lambda-{}^1/_2 r^2\lambda^2 P_r+\alpha P_r/8\pi,$$
$$P_s\approx{}^1/_2 P_\lambda-{}^1/_2 r^2\lambda^2 P_r+{}^1/_2\lambda r P_\lambda-{}^1/_2 P_\lambda+B+\alpha P_r/8\pi, \quad (15)$$

where

$$P_\lambda=\lambda\int_0^\infty P(z')e^{-\lambda z'}dz', \quad P_r=\int_0^\infty P(z')e^{-z'/r}dz'/r.$$

Since the relation between the parameters $r\lambda$ and $\alpha/4\pi$ can be arbitrary, it follows from the first equation of (15), which is equivalent to (12), that either $B\sim r\lambda P_\lambda$, or $B\sim\alpha P_r/8\pi$. The second estimate in (15) shows that the correct solution is the first and $B\sim r\lambda P_\lambda$. In this case $P_r\sim\lambda r P_\lambda\ll P_\lambda$. Taking into account these estimates, we can write for B the expression

$$B=\frac{r\lambda^2}{2}\int_0^\infty P(z')e^{-\lambda z'}dz'. \quad (16)$$

We note that inasmuch as by virtue of these estimates in (13) and (14) the main contribution to the integral in (16) is made by the region $z\sim 1/\lambda$ but not by the smaller region $z\lesssim r\ll 1/\lambda$, it follows that (16), accurate to within the small parameter (13), is not an equation for B (or P), but determines the solution of (14) in the region $z\ll 1/\lambda$ in terms of the parameters of the solution in the region $z\sim 1/\lambda$. In this region, the equation for $P(z)$ takes, as follows from (14), the following form:

$$-2\pi\lambda\int_0^\infty\exp(-\lambda|z-z'|)P(z')dz'+4\pi P(z)$$
$$+2\pi\lambda e^{-\lambda z}\int_0^\infty P(z')e^{-\lambda z'}dz'=-\frac{\partial f(P)}{\partial P}. \quad (17)$$

It turns out that the solution (9) can be continued into the region $z\sim 1/\lambda$, where it should satisfy also Eq. (17). The requirement that the solutions be matched leads then to the condition

$$\bar P''(0)=-\bar P(0)\lambda^2, \quad (18)$$

where $\bar P(z)$ is the solution of Eq. (6), including also in the region $z<1/\lambda$. In (18) the values of $\bar P(z)$ were taken at $z=0$ by virtue of the fact that the characteristic lengths over which the solution (9) varies is much larger than $1/\lambda$, so that we can put with good accuracy $z=0$.

The condition (8) can be easily rewritten with the aid of (9) in the form:

$$\partial f(\bar P)/\partial\bar P+4\pi\bar P=0. \quad (19)$$

In experiment usually $|\partial f/\partial P|\ll P$ at all $|P|\lesssim P_0$. In this case (19) has a unique solution $\bar P=0$. However, (19) can have also other solutions, from which it is necessary to choose the one corresponding to the minimum of the free energy. We confine ourselves here to a case when the solution is unique: $\bar P=0$.

Thus, the solution in the region $z\gtrsim 1/\lambda$ is of the form

$$\int_0^P\frac{dP'}{(2[f(P')-f(P_0)])^{1/2}}=\rho z, \quad (20)$$

and in the region $z\ll 1/\lambda$

$$P(z)=\int_0^\infty K(z')G_1(z-z')dz'+Be^{-z/r},$$
$$K(z)=-4\pi\lambda^2 z\int_0^\infty P(z')\exp(-\lambda z')dz', \quad (21)$$

and in the integrals that determine B and K in (21) it is necessary to replace $P(z)$ by the solution (20). The expression (21) can be easily obtained from (14) in the limit $z\to 0$.

The function $F(P)$ is invariant to the replacement of P by $-P$ and has therefore an extremum at $P=0$. We consider the case when this is a maximum, which is realized if the ferroelectric undergoes a second-order phase transition. Then (9) at small P takes in the region $z>r$ the form

$$P=(2[f(0)-f(P_0)]/\alpha_2)^{1/2}\sin[\alpha_2^{1/2}\rho z],$$
$$\alpha_2=-\frac{\partial^2 f}{\partial P^2}\Big|_{P=0}. \quad (22)$$

We note that an important factor in the derivation of the boundary conditions (12) and (18) was the use of the fact that $\varkappa\neq 0$. If we were to assume $\varkappa=0$ from the very outset, as is sometimes done in the case of small r, then the boundary condition which is the analog of (18) would have to be found from the condition that the free energy be a minimum. This procedure, as can be shown, leads to Eq. (20) for $P(z)$ and consequently makes it possible to obtain the correct solution only in the region $z>r$.

It is also of interest to note that $P_s=P(0)$ is a small quantity not of the order of αP_0, as might be expected, but of the order of $r\lambda\alpha^{1/2}P_0$, which generally speaking may be larger than αP_0.

We consider now the case inverse to (13):

$$\varkappa\lambda^2/4\pi\gg 1, \quad (23)$$

when the smallest length in the problem is $1/\lambda$, and the change of $P(z)$ near the boundary is determined by the screening by the intrinsic carriers. The estimates analogous to (15) assume here the form

$$B=-P_\lambda/r\lambda+{}^1/_2 P_r+\alpha P_r/8\pi,$$
$$P_s=B-P_\lambda/2r^2\lambda^2+{}^1/_2 P_r-P_\lambda/2r\lambda+P_\lambda/2r^2\lambda^2+\alpha P_r/8\pi. \quad (24)$$

The investigation of (24) is more cumbersome than that of (15), because of the larger number of solutions that must be verified. We write out directly the answer, the validity of which can be checked by direct substitution. In the region $z\lesssim 1/\lambda$

$$P\approx A_0+A_1 z+A_2 e^{-\lambda z},$$
$$A_2=4\pi A_0/\varkappa\lambda^2, \quad A_1=4\pi A_0/\varkappa\lambda. \quad (25)$$

Matching (25) to the solution in the region $z\gg 1/\lambda$, which satisfies as before Eq. (6), leads to the following boundary condition—the analog of (18)—for the long-wave part of the solution in the region $z\sim 1/\lambda$:

$$\bar P'(0)=\bar P(0)\cdot 4\pi/\varkappa\lambda. \quad (26)$$

In (26), for the same reasons as in (18), we put $z=0$, while $\bar P(z)$ in (26), just as in the derivation of (20) from

(9), satisfies Eq. (6). Bearing this in mind, we easily obtain from (26) the following equation for $\tilde{P}(0)$:

$$[f(\tilde{P})-f(P_0)]^{1/2}=4\pi\tilde{P}/\varkappa^{1/2}\lambda. \quad (27)$$

Since the relation between the parameters α and $\varkappa\lambda^2/4\pi$ [the latter satisfies (23)] can be arbitrary, Eq. (27) can with full justification have solutions even of the order of P_0. It is necessary for this purpose that the Debye radius $1/\lambda$ be small enough. It is easy to show that in this case the solution at $z>1/\lambda$ takes the form (10).

Using the obtained equations for $P(z)$ and Eq. (4) we easily obtain the restrictions needed to make the band bending small, as assumed. In the case (13), for example, this requirement leads to the inequality

$$qP_0(4\pi\alpha)^{1/2}\ll\lambda kT.$$

3. CONCLUSION

The polarization field can be screened also by charges in the surface states. In the case when $P=P_0$ all the way to the surface, the charge density for complete screening should be equal to P_0. However, the surface-state levels can be located outside the volume forbidden band or near its boundaries.[9] Then their contribution to the screening of the polarization field is negligible.

There exist, of course, also inverse situations, when the surface-state bands are sufficiently narrow and lie close to one another in the volume forbidden band. The displacement of the Fermi level on the surface is in this case limited by the dimensions of the surface bands and by the distance between them. In this case practically the entire screening is produced by the charges in the surface states. Such a picture, however, is far from always observed: on the surfaces of covalent semiconductors (Si, Ge), on contacts of individual semiconductors with metals, when submonolayers of certain substances are evaporated on semiconductors, etc.[9] On the other hand, in ionic semiconductors the influence of the surface states on the screening is small,[9] although even here the appearance of vacancies or of an excess of atoms on the surface as the result of some process can lead to formation of surface states in the forbidden band.

Little is known on surface states in ferroelectrics, but by analogy with other ionic wide-band substances[9] it can be assumed that in a semiconducting ferroelectric the first variant is more probable, and the influence of the surface states is small.

We emphasize in conclusion that the boundary condition for the polarization on the boundary of a semiconducting ferroelectric, a condition needed for a correct formulation of the boundary-value problem, is a simple consequence of the requirement (12) that the free energy be small, or can be obtained from this requirement in a more complicated manner in the case $\varkappa=0$. A study of the screening of the spontaneous-polarization field by free carriers has shown that the polarization in the field on the boundary of a semiconducting ferroelectric are generally speaking not equal to zero, as had been assumed previously, and their actual values are determined by the requirements that the free energy be minimal. A change of P_s involves a change of the polarization and of the field near the surface of the semiconducting ferroelectric.

We note also that the character of the change of the polarization near the surface of the semiconducting ferroelectric is determined not by one length, as might be expected, but by two lengths; the minimal length determines the dimensions of some transition layer in which the polarization varies with distance much more rapidly than in the principal layer [see, e.g., (20) and (21)].

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