Ferroelectric thin film properties with account of metallic electrodes and depolarization field influence

M. D. Glinchuk and B. Y. Zaulychny

Institute for Problems of Materials Science, National Academy of Sciences of Ukraine

V. A. Stephanovich

Institute of Mathematics and Informatics, University of Opole, 45-052 Opole, Poland

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Within the framework of the phenomenological Ginzburg-Landau theory influence of metallic electrodes on the properties of thin ferroelectric films is considered. The contribution of the metallic electrodes with different screening length of carriers is included in functional of free energy.

The influence of conventional metallic electrodes on the depolarization field and the film properties was shown to be practically the same as for superconductive ones.

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Influence of electrodes on properties of thin ferroelectric films attracts much attention from scientists and engineers. It is related to substantial influence of electrodes on the field of depolarization, and also with the necessity of proper electrodes types (superconductor, metal, semiconductor) choice which is optimal for applications. The field of depolarization plays essential role in the physics of ferroelectrics, because it tries to destroy spontaneous electric polarization and so ferroelectric phase. It is known that such internal factors as domain structure and free carriers partly diminish the field of depolarization. The external factors, namely electrodes, can substantially decrease the field of depolarization. For example, superconductive electrodes in the bulk ferroelectrics lead to complete compensation of the depolarization field. In thin ferroelectric films due to inhomogeneity of the polarization related to the contribution of surface effects, there is only partial compensation of the depolarization field even for superconductive electrodes \( \ddagger \). The account of metallic electrodes influence resulted in the necessity of including the contribution of electrodes into free energy, which appeared considerably more difficult for the case of non-superconductive electrodes (see \( \| \) and references therein). Because of this up to now the calculations of non-superconductive electrodes influence on the properties of thin ferroelectric films were not carried out.

In this work we made these calculations in the model of monodomain ferroelectric material treated as an ideal insulator. This model is realistic enough, as with diminishing of film thickness it becomes a monodomain one \( \mathbb{R} \) and in majority of ferroelectrics conductivity is very small (see for example \( \mathbb{L} \)). The calculations of metallic electrodes contribution into free energy functional were performed by the way firstly proposed in \( \mathbb{I} \), however corrections of the formulae obtained in \( \mathbb{I} \) have been made.

We will consider thin ferroelectric film between two metallic electrodes (Fig. 1). Taking into account that monodomain films selfpolarized in the normal direction to the surface technologically can be produced \( \mathbb{R} \), we will examine the film polarized along the axis of \( z \) (i.e. \( P = P_z \neq 0, P_x = P_y = 0 \)).

The equilibrium values of polarization can be obtained within the framework of phenomenological theory from the condition of free energy functional minimum. We will write down free energy as a sum of free energy of film, including the field of depolarization, and electrodes. It is known that the field of depolarization is oppositely directed to spontaneous polarization and so aims to destroy it. In the accepted model of monodomain film without the carriers only electrons in electrodes can decrease the field of depolarization. This effect is maximal for super-
Conductive electrodes. For non-superconductive metallic electrodes Thomas-Fermi screening of the carriers has to be taken into account, so that the field in an electrode satisfies the equation:

\[
\frac{d^2E}{dz^2} = \frac{1}{\ell_s^2} E \quad (1a)
\]

where screening length \( \ell_s \) has the form:

\[
\ell_s^2 = \frac{1}{4\pi e^2 D(E_f)} \quad (1b)
\]

Here \( e, D(E_f) \) is charge and density of orbital states of carriers on Fermi energy level respectively.

It is seen that because of the wide values interval of \( D(E_f) \) in metals, value of \( \ell_s \) can change from \( \ell_s = 0 \) (superconductor) to units of angstrom. One can expect that with increase of \( \ell_s \) contribution of electrodes to decrease of the depolarization field will diminish.

For quantitative consideration of electrodes influence on film properties we will find the contribution of electrodes to decrease within the whole system:

\[
E(z) = \begin{cases} 
\frac{L}{2}, & -\frac{L}{2} \leq z \leq -\frac{L}{2} \\
0, & \frac{L}{2} \leq z \leq \frac{L}{2} 
\end{cases} \quad (7)
\]

In order to find \( E_0 \) we must account for influence of external voltage \( V_0 \), namely:

\[
\int_{-L/2}^{L/2} E(z) \, dz = -V_0 \quad (8)
\]

After substitution of Eq. (7) into Eq. (8) we obtain \( E_0 \) in the form:

\[
E_0(z) = \frac{1}{2\alpha l_2+1} \left[ 4\pi \int_{-L/2}^{L/2} Pdz - V_0 \right] \quad (9)
\]

Note, that multiplier \( 1/\varepsilon_e \) was omitted in [2]. The obtained expression for \( E_0 \) defines completely electric field in the film (see Eq. (5)) and in the electrodes (see Eqs. (6) (9)).

We can express density of free energy of the film as

\[
F_e = \frac{2}{8\pi} \int_{-L/2}^{-1/2} \frac{d^2 E}{dz^2} dz = \frac{2\pi Q^2 l_1 \beta}{8\pi (L-l)} = \frac{E_0^2 l_1 \beta}{8\pi (L-l)} \quad (10)
\]

The density of free energy of the film can be written in conventional form for the ferroelectrics with the second order phase transition:

\[
F_f = \frac{1}{4} \int_{-L/2}^{L/2} dz \left\{ \frac{1}{2} AP^2 + \frac{1}{4} B P^4 + \frac{1}{2} C \left( \frac{dP}{dz} \right)^2 - E(z) P - 2\pi P^2 \right\} + \frac{c_0^2}{2L} \left( P^2 \left( -\frac{2}{7} \right) + P^2 \left( \frac{L}{2} \right) \right) \quad (11)
\]
Here \( A = A_0(T - T_c), \) \( T_c \) and \( A_0 \) is a temperature of ferroelectric transition in the bulk and the inverse constant of Curie-Weiss respectively, \( \delta \) is extrapolation length.

Finally, after substitution Eqs. (9, 10) into Eq. (11) we get explicit expression for total density of free energy of the system:

\[
F = \frac{F_s(S_l-S_f)}{2L} = \\
\frac{1}{2} \left[ \int_{-l/2}^{l/2} dz \left\{ \frac{1}{2} AP^2 + \frac{1}{4} BP^4 + \frac{1}{2} C (\frac{dP}{dz})^2 + \\
\frac{V п}{(2a_0+1)} - \frac{V п}{2(2a_0+1)} + \frac{2\pi P^2}{L(2a_0+1)^2} \right\} + \frac{2\pi(P)^2 l_\beta \beta^2}{2(2a_0+1)^2} + \frac{V п l_\beta}{8sL(2a_0+1)^2} \right].
\]

Variation of functional (12) leads to the Euler-Lagrange equation for polarization and to boundary conditions of the following form:

\[
AP + BP^3 - C \left( \frac{dP}{dz} \right) = E_{ext} + E_d
\]

\[
E_{ext} = -\frac{V п}{a} \quad E_d = -4\pi (P - a P)
\]

\[
a = l \left( \frac{1}{(2a_0+1)} - \frac{l_\beta}{(2a_0+1)^2} \right)
\]

\[
\frac{dP}{dz} \bigg|_{z=\pm \frac{l}{2}} = \mp \frac{P(\pm \frac{l}{2})}{\delta}
\]

The Eq. (12a) for superconductive electrodes \((l_s \to 0, a \to 1)\) coincide with expression obtained earlier in [1, 9, 10], while the expression for \(E_d\) derived from formulae in [2] contains multiplier \(1/\varepsilon_f\) \((\varepsilon_f\) is dielectric permittivity of the film). That decrease essentially the \(E_d\) value for arbitrary \(P(z)\) values. In general case \(a < 1\) for conventional metallic electrodes so that depolarization field increase.

However, it is easy to see that parameter \(a \approx 1\) for metallic electrodes, because \(l_s \ll l\) and at \(\varepsilon_e \geq 10^4, \alpha \approx \beta \approx 10^{-4}\) thus metallic electrodes for wide range of metalls (Au, Al, Pt) act like superconductive ones. Therefore the results of calculations of ferroelectric thin film properties performed for the superconductive electrodes in our previous papers [3], [10] will be applicable for any metallic electrodes. In particular calculations of \(P(z)\) and \(P\) in [10] had shown that in the middle part of the film \(E_d \approx -4\pi P/\varepsilon_f\) so that electrodes do decrease the depolarization field. It is expected that semiconductor electrodes which have larger \(l_s\) value and much smaller \(\varepsilon_e\) will lead to larger depolarization field and so to the decrease of spontaneous polarization and to the increase of critical thickness of phase transition from ferroelectric to paraelectric phase. For quantitative consideration of such electrodes the account of zone bend and effects related to the spatial charge is needed (see [11]). These calculations are in the progress now.

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[1] R. Kretchmer and K. Binder, Phys.Rev.B 20, 1065 (1979).
[2] D. Tilley (1996), ed. With. Paz de Araujo, J.F. Scott, G.W. Taylor, Gordon and Breach, Amsterdam.
[3] A. Bratkovsky and A. Levanyuk, Phys.Rev.Lett. 84, 3177 (2000).
[4] G. Suchaneck, T. Sander, R. Kohler, and G. Gerlach, Integrated ferroelectrics 27, 127 (1999).
[5] G. Pike, W. Warren, D. Dimos, B. Tuttle, R. Rames, J.Lee, V. Keramidas, and J. Evans, Appl.Phys.Lett. 66, 484 (1995).
[6] R. Bruchaus, D. Pitzer, R. Primig, M. Schreiter, and W. Wersing, Integrated ferroelectrics 25, 1 (1999).
[7] V. M. Frydkyn (1978), Ferroelectrics-semiconductors. Nauka, Moscow.
[8] S. Kittel (1987), Introduction to physics of solid. Mir. Moscow.
[9] M. Glinchuk, E. Eliseev, and V. Stephanovich, Physica B 322, 356 (2002).
[10] M. Glinchuk, E. Eliseev, V. Stephanovich, and R. Farhi, J.Appl.Phys. 93, 1150 (2003).
[11] I. Batra, P. Wurfel, and B. Silverman, Phys.Rev.Lett. 30, 384 (1973).