PHYSICAL REVIEW B VOLUME 8, NUMBER 7 1 OCTOBER 1973

Phase Transition, Stability, and Depolarization Field in Ferroelectric Thin Films

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(Received 14 March 1973)

It is shown that the polarization in a thin ferroelectric film, which is sandwiched between semiconducting electrodes, is compensated incompletely. The associated depolarization fields are size dependent and change the magnitude of the polarization, transition temperature, coercive field, and the order of the phase transition. Thermodynamic considerations give stability requirements for thin films, which are different from the bulk. The properties of a thin ferroelectric film, which in bulk form exhibits a second-order phase transition, are investigated as a function of thickness, temperature, biasing potential, and electrode properties. Numerical results are presented for triglycinesulfate.

I. INTRODUCTION

In the phenomenological formulation of the theory of phase transitions by Landau,[1] a second-order transition is described by an expansion of the free energy in terms of an order parameter up to fourth order (where the fourth-order term is positive) while a first-order transition follows from an expansion up to sixth order (where the fourth-order term is negative). Some authors[2,3] have recently discussed the origin of the order of a phase transition. Anderson and Blount[2] have pointed out that a first-order transition is possible in an expansion up to fourth order when strain is involved since the third-order term in strain does not generally vanish in the free-energy expansion. Pytte as well as Gillis and Koehler[3] have discussed the results of model calculations that go beyond the Landau theory. They conclude that the self-consistent-field theory can lead to a first-order transition when the only anharmonicity is of fourth order. In a recent brief communication[4] we proposed a new type of first-order phase transition in a ferroelectric resulting from Landau's theory by considering only terms up to fourth order in the polarization but the fourth-order term is positive. The purpose of this article is to present the detailed formulation and further implications. It has been shown[4] by considering a unidomain ferroelectric thin film sandwiched between semiconducting electrodes that the order of a phase transition can be size dependent. The change of the order of the transition results from the distribution of the charge in the semiconducting electrodes which compensates the ferroelectric polarization.

For a unidomain ferroelectric the compensation of the polarization by external charges is vital. Without compensation usual values of polarization of about 1 $\mu C/cm^2$ lead to fields ~10^7 V/cm inside the ferroelectric opposite to the polarization and under these conditions ferroelectricity is thermodynamically unstable. For its stability, charges and their distribution in electrodes are important. The usual thermodynamic theory neglects electrode effects by assuming a large volume of the ferroelectric. In thin ferroelectric films, however, the electrode properties and details of charge distribution play an important role. It is realized[5-7] that in thin films the polarization is not completely neutralized by external charges and fields opposite to the polarization, called depolarization fields, are present.

The existence of depolarization fields can be physically understood from Fig. 1, which shows the potential V in a ferroelectric ($\infty \times \infty \times l$) of thickness l in contact with two semiconducting electrodes. Owing to the low spacecharge density in semiconductors, the charge neutralizing the polarization is spread over a certain distance from the interface. The field from the surface of the ferroelectric penetrates over this

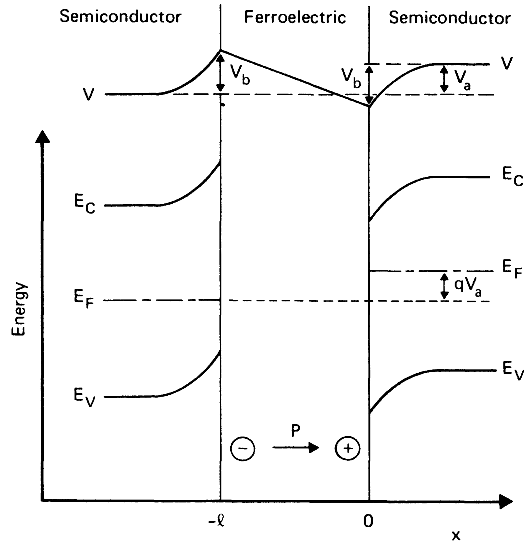

FIG. 1. Distribution of potential V in a ferroelectric-semiconductor configuration.

distance into the electrodes which causes a potential drop or band bending in the electrodes. The band bending V_b gives rise to the depolarization field in the ferroelectric which under short-circuit conditions is essentially the sum of the band bending in the electrodes divided by the thickness l of the ferroelectric. Large depolarization fields result when l becomes small and the polar state can be completely destroyed. The depolarization field indicates that there is a lack of compensation, which is a consequence of electrode properties and circuit conditions.

In what follows we will examine the influence of depolarization fields on the properties of a thin ferroelectric film including the order of a phase transition. The stability considerations based on thermodynamic free-energy calculations will be thoroughly discussed. The ferroelectric is assumed to be a perfect dielectric with homogeneous polarization compensated by charges in the electrodes only. Inferface states are neglected in our calculation but densities $\lesssim 10^{12}/\text{eV cm}^2$ would not alter our conclusions.

II. THEORY

Consider a ferroelectric sandwiched between two semiconducting electrodes subject to a biasing potential V_a. The energy-band diagram for such a system is shown in Fig. 1. Owing to V_a, the Fermi levels E_F in the two electrodes are relatively displaced by qV_a, where q is the magnitude of the electronic charge. When the ferroelectric is uniformly polarized (the polarization direction as indicated in Fig. 1 is taken to be positive), compensation charges accumulate near the interfaces resulting in bending conduction E_c and valence E_v bands in the electrodes. In the upper part of Fig. 1, the electrostatic potential V is shown and the band bending V_b which is responsible for the depolarization field in the ferroelectric is indicated. The field E_f in the ferroelectric is determined by V_a and V_b. For a ferroelectric, which in bulk form exhibits a second-order phase transition and is under the influence of a macroscopic electric field E_f, the free-energy density $F(T, P)$ is[1,8,9]

$$F(T, P) = F_0 + \tfrac{1}{2} aP^2 + \tfrac{1}{4}\xi P^4 - \int_0^P E_f\, dp\,, \tag{1}$$

where F_0 is the free-energy density in the unpolarized state, $a\ [\equiv 4\pi(T - T_0)/C]$ and ξ are the usual expansion coefficients, T_0 is the bulk transition temperature, and C is the Curie constant. From Fig. 1 it is clear that due to the field penetration into the electrodes there is electrostatic energy stored in the electrodes as well, which has to be included in the total free energy of the ferroelectric-semiconductor system. The total free energy per unit area is

$$F(T, P)\,l = l\left(F_0 + \tfrac{1}{2} aP^2 + \tfrac{1}{4}\xi P^4 - \int_0^P E_f\, dp\right) + \frac{\epsilon}{4\pi}\int_0^\infty E_e^2(x)\, dx\,, \tag{2}$$

where $E_e(x)$ is the electric field in the electrodes of dielectric constant ϵ. A factor of 2 has been included in the electrode energy term since there are two identical electrodes.

The field in the ferroelectric follows from the continuity of the displacement vector at the interface and is

$$E_f = 4\pi(\rho_0 - P)\,, \tag{3}$$

where ρ_0 is the total charge per unit area in each electrode. Since this field is spatially uniform, it immediately follows from Fig. 1 that

$$E_f l = V_a - 2V_b\,, \tag{4}$$

from which E_f can be computed if the band bending V_b is known. A negative value of E_f results in depolarization.

The band bending in the intrinsic semiconducting electrodes is calculated from Poisson's equation

$$\frac{dE}{dx} = -\frac{4\pi q}{\epsilon}\,[n(x) - n_i - p(x) + n_i]\,, \tag{5}$$

where n and p are electron and hole concentrations, respectively, and n_i is the intrinsic carrier density. The impurity concentration is assumed to be negligible compared with the concentration of free carriers. As will be seen $V_b \gg kT/q$ and thus $p(x)$ can be neglected for electron accumulation and $n(x)$ for hole accumulation. This coupled with the Boltzmann statistics $n(x) = n_i\, e^{qV(x)/kT}$ gives an equation[10] for the electric field distribution in the electrodes which can be readily solved to obtain

$$E_e(x) = \frac{4\pi}{\epsilon}\,\rho_0\left(1 + \frac{x}{2d}\right)^{-1}, \quad x \geq 0 \tag{6}$$

where $d \equiv \epsilon kT/4\pi q\rho_0$. The carrier distribution in the electrode for accumulation then is

$$n(x) = n_R\left(1 + \frac{x}{2d}\right)^{-2}, \quad x \geq 0 \tag{7}$$

where $n_R \equiv \rho_0/2qd$ is the charge density at the interface. For $\rho_0 = 1\ \mu\text{C/cm}^2$ at room temperature $n_R \simeq 2\times 10^{20}/\text{cm}^3$ and $d \simeq 1.5$ Å.

The band bending in each electrode is

$$V_b = \frac{kT}{q}\ln\left(\frac{n_R}{n_i(T)}\right) \equiv \frac{kT}{q}\ln\left(\frac{2\pi\rho_0^2}{\epsilon n_i(T) kT}\right)\,, \tag{8}$$

and the intrinsic carrier concentration $n_i(T)$ of a semiconductor is related to its band gap E_g by

$$n_i(T) = N_0\, e^{-E_g/2kT}\,, \tag{9}$$

where N_0 is the effective density of states which is assumed to be equal for conduction and valence bands.

The requirement that the band bending $V_b \gg kT/q$, which enabled us to neglect the minority carriers, can now be formulated as the condition $[2\pi\rho_0^2/\epsilon n_i(T)kT] \gg 1$, which for $n_i = 10^{16}/\mathrm{cm}^3$ at room temperature is satisfied if $\rho_0 > 7\times10^{-3}\ \mu\mathrm{C/cm}^2$. Since $\rho_0 \simeq P$, usual values of ρ_0 are on the order of 1 μC/cm^2, and the above condition is always satisfied. For a typical value of ρ_0 of 1 μC/cm^2, the concentration of carriers at the interface $n_R \simeq 2\times10^{20}/\mathrm{cm}^3$ is degenerate and it might be argued that one should use Fermi-Dirac statistics. However, the deviations from Boltzmann statistics occur only in a layer of a few angstroms at the interface (the characteristic length d for the carrier distribution is 1.5 Å) and the resulting changes in the band bending are small. Furthermore, one knows that the effect of Fermi statistics is to lower the interface charge density and consequently increase the band bending. This can only emphasize the effects under consideration but the essential physics remains unaltered.

The field E_f in the ferroelectric from Eqs. (4) and (8) is

$$E_f = \frac{V_a}{l} - \frac{2kT}{ql}\ln\left(\frac{2\pi\rho_0^2}{\epsilon n_i kT}\right), \tag{10}$$

and using Eq. (3) we find the relation between ρ_0 and P:

$$P = \rho_0 + \frac{kT}{2\pi q l}\ln\left(\frac{2\pi\rho_0^2}{\epsilon n_i kT}\right) - \frac{V_a}{4\pi l}. \tag{11}$$

The electrostatic energy in the electrodes follows from Eq. (6) and is

$$\frac{\epsilon}{4\pi}\int_0^\infty E_e^2(x)\,dx \simeq \frac{\epsilon}{4\pi}\int_0^{x_i} E_e^2(x)\,dx = \frac{2kT}{q}\rho_0. \tag{12}$$

The integration is terminated at x_i where $n(x_i) = p(x_i) = n_i$, because that is the limit of validity of our assumption that minority carriers can be neglected. For computing the energy associated with E_f in the ferroelectric, recall[9] that the polarization P is stable only for $E_f \lesssim 10^5$ V/cm when E_f is opposite to P. Since for usual values of P of 1 μC/cm^2 without compensation the depolarization field is $E_f = 10^7$ V/cm, we see that for stable polarization values the compensation charge ρ_0 can at most differ by 1% from the polarization P. Therefore we replace ρ_0 by P in Eqs. (10) and (12) and find the total free energy per unit volume of the ferroelectric to be

$$F = F_0 + \frac{2\pi}{C}(T - T_0)P^2 + \tfrac{1}{4}\xi P^4 - P V_a/l + \frac{2kT}{ql}P\left[\ln\left(\frac{2\pi P^2}{\epsilon n_i(T)kT}\right) - 1\right]. \tag{13}$$

To obtain equilibrium polarization values and their stability as a function of ferroelectric film thickness, applied voltage, and temperature, we need at least the first and second derivatives of the free-energy function with respect to P. These can be obtained directly from Eqs. (2) and (10)–(12) without approximating ρ_0 by P and are

$$\frac{\partial F}{dP} = \frac{4\pi}{C}(T - T_0)P + \xi P^3 - V_a/l + \frac{2kT}{ql}\left[\ln\left(\frac{2\pi\rho_0^2}{\epsilon n_i kT}\right) + \frac{1}{1+\delta}\right], \tag{14}$$

$$\frac{\partial^2 F}{dP^2} = \frac{4\pi}{C}(T - T_0) + 3\xi P^2 + \frac{2kT}{ql\rho_0}\left(\frac{2}{1+\delta} + \frac{1}{(1+\delta)^2} - \frac{1}{(1+\delta)^3}\right), \tag{15}$$

where $\delta = kT/\pi q l \rho_0$ and is generally very small compared with unity (for $\rho_0 = 1\ \mu\mathrm{C/cm}^3$ at $T = 300\ ^\circ\mathrm{K}$ and $l = 10^{-5}$ cm, $\delta \simeq 10^{-3}$). Equilibrium solutions (absolutely stable and metastable) for the polarization must satisfy the conditions

$$\frac{\partial F}{\partial P} = 0 \tag{16}$$

and

$$\frac{\partial^2 F}{dP^2} > 0. \tag{17}$$

Equations (16) and (11) can be solved simultaneously to obtain equilibrium values for the polarization as a function of film thickness l, applied voltage V_a, and temperature T. The stability of these equilibrium solutions is then checked in Eq. (17). Solutions which satisfy Eq. (17) are stable because they belong to a minimum of the free energy. A solution is absolutely stable if it belongs to the lowest minimum in free energy. Solutions which are stable but not absolutely stable are called metastable which means that there is another minimum for which the free energy has the same or a lower value. Unstable solutions are obtained when $\partial^2F/\partial P^2 < 0$ and the phase transition is a result of this instability condition. It should also be remarked that due to the nonlinear nature of the equations, analytical solutions for ρ_0 and P cannot be obtained. Numerical solutions and the physical interpretation of the results are presented in Sec. III.

III. RESULTS AND DISCUSSION

Since the free-energy function of the ferroelectric-semiconductor system is nonlinear, solutions can only be obtained by numerical methods. For computations and discussion of physical results we chose triglycinesulfate (TGS), a typical ferroelectric which in bulk form exhibits a second-order phase transition. Its material constants are: $T_0 = 49.8\ ^\circ\mathrm{C}$, $\xi = 8.0\times10^{-10}\ (\mathrm{esu/cm}^2)^{-2}$ and $C = 3300\ ^\circ\mathrm{C}$.

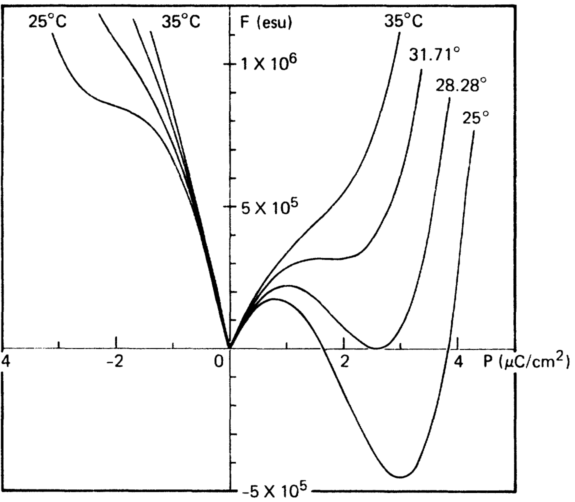

FIG. 2. Free energy F of a ferroelectric TGS film 10^{-5} cm thick with semiconducting electrodes, as a function of polarization P at an applied voltage $V_a = 0.25$ V for several values of temperature.

Parameters characterizing the semiconducting electrodes are taken as: dielectric constant $\epsilon = 6$, effective density of states $N_0 = 10^{19}/\text{cm}^3$, and band gap $E_g = 0.69$ eV.

It is instructive to examine the free energy of the ferroelectric-semiconductor system. The free-energy function is given in Eq. (13) and plotted in Fig. 2 as a function of P for a 10^{-5}-cm-thick TGS film subject to a biasing potential $V_a = 0.25$ V for several values of temperature. For convenience we set $F_0 = 0$. A comment is in order for the small-P regime ($|P| \lesssim 10^{-3}$ μC/cm^2) since the equations derived in this paper are for the strong-space-charge-deviation condition and strictly speaking not valid in the small-P regime. We shall not pay much attention to this uninteresting regime except from noting that the screening-length approximation[7] is more appropriate which contributes a term $\sim P^2$ in the free-energy expression instead of the logarithmic term in Eq. (13). This would then lead to a minimum in the free energy at $P = 0$. From Fig. 2 we see that at 25 °C there is an absolutely stable nonzero solution for the polarization because of the absolute minimum of the free energy. At 28.28 °C there is a nonzero solution just on the metastability limit because the free energy at this P value is equal to the free energy at $P \cong 0$. At $T > 28.28$ °C the solution for P is metastable, until at $T = 31.71$ °C it becomes unstable because at $T \geq 31.71$ °C for $V_a = 0.25$ V there is not even a relative minimum in the free energy at $P > 0$. At $T = 31.71$ °C the polarization is on the stability limit which separates metastable and unstable solutions for P. Although we started out with a second-order bulk ferroelectric, the behavior of the free energy of the ferroelectric-semiconductor system shown in Fig. 2 is typical for first-order transitions. We have found a new type of first-order transition which arises from the interaction of a thin ferroelectric with its semiconducting electrodes.

To trace the origin of this first-order transition, we plot in Fig. 3 the usual part, F_n, of the free-energy function, the part, F_e, associated with the electrodes, and the total $F \equiv F_e + F_n$. Here

$$F_n = \tfrac{1}{2} aP^2 + \tfrac{1}{4} \xi P^4 - P V_a / l , \tag{18}$$

$$F_e = \frac{2kT}{ql} P \left[\ln\left(\frac{2\pi P^2}{\epsilon n_i(T) kT} \right) - 1 \right] , \tag{19}$$

where F_0 has been set equal to zero. From Eq. (19) it is clear that for bulk ferroelectrics ($l \rightarrow \infty$) $F_e \rightarrow 0$ and then F_n gives the usual second-order phase transition since $\xi > 0$. The term F_e becomes important for thin ferroelectric films and is nearly linear in P. As stated earlier, the expression for F_e is not rigorously correct in a small regime around $P = 0$. The total free energy for a 10^{-5}-cm-thick TGS film in contact with semiconducting electrodes shown in Fig. 3 rises at small values of P due to the F_e term, reaches a maximum value, and then becomes negative ($a < 0$) due to the P^2 part of F_n, and after going through a minimum rises to

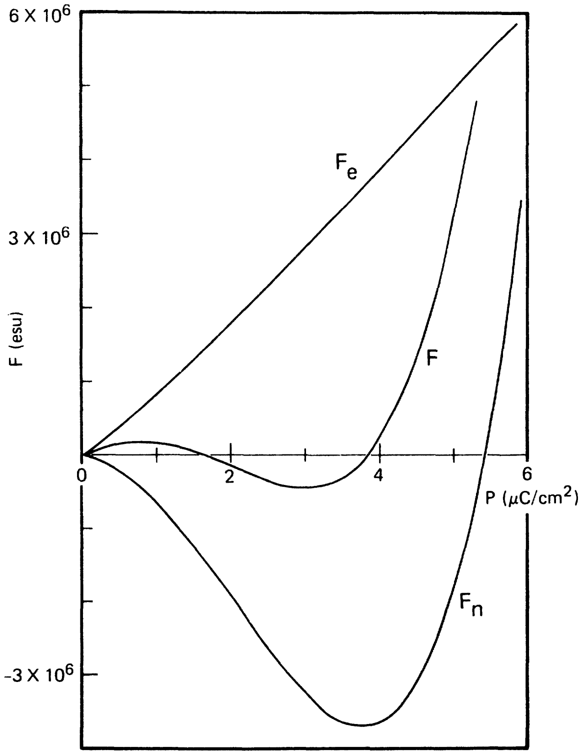

FIG. 3. Contributions of intrinsic free energy F_n of a TGS film 10^{-5} cm thick and of electrode effects F_e to the total free energy F at 25 °C and $V_a = 0.25$ V.

positive values ($\xi > 0$) due to the P^4 contribution. Such behavior predicts a first-order phase transition and the term F_e is responsible for it. With increasing l the relative contribution of F_e decreases, eventually the minimum near $P = 0$ disappears and the transition becomes of the second order. It should be emphasized that the functional dependence of the compensating charge is responsible for the modification of the order of the transition.

Now let us examine the dependence of polarization on external parameters. Basically there are four variables, namely, temperature, length, biasing potential, and band gap or intrinsic carrier density upon which polarization depends. One could plot P as a function of one of these variables holding the other three fixed. In what follows E_g [or $n_i(T)$] will be used strictly as a parameter and l, T, and V_a dependence will be more thoroughly investigated. These results are obtained by solving Eqs. (11) and (16) simultaneously using a iterative numerical technique due to Muller.[11]

The polarization as a function of thickness under short-circuit conditions ($V_a = 0$) for $E_g = 0.69$ and 0.35 eV is shown in Fig. 4 at two different temperatures. The higher band gap gives $n_i = 10^{13}/\text{cm}^3$ at 300 °K which is realized in germanium. The lower band gap gives $n_i = 10^{16}/\text{cm}^3$ at room temperature, a value not too different from tellurium. It is seen that the polarization decreases with decreasing thickness and at any finite thickness lies below the bulk value P_s. The transition from nonzero to zero polarization is abrupt again indicating the "first-order behavior" of the ferroelectric-semiconductor system. In reducing the thickness of the ferroelectric, the transition occurs when nonzero values become metastable and zero values absolutely stable. One solves for this transition length l_c by setting $F = 0$ along with Eqs. (11) and (16). Physically this means that at $l = l_c$ the free energy of the polar state is equal to the free energy of the nonpolar state. Any further reduction of l raises the free-energy density of the polar state making it energetically less favorable. Consequently, a transition occurs at l_c. The curve for $n_i = 10^{16}/\text{cm}^3$ lies above the curve for $n_i = 10^{13}/\text{cm}^3$ because the higher carrier concentration provides better compensation of the polarization.

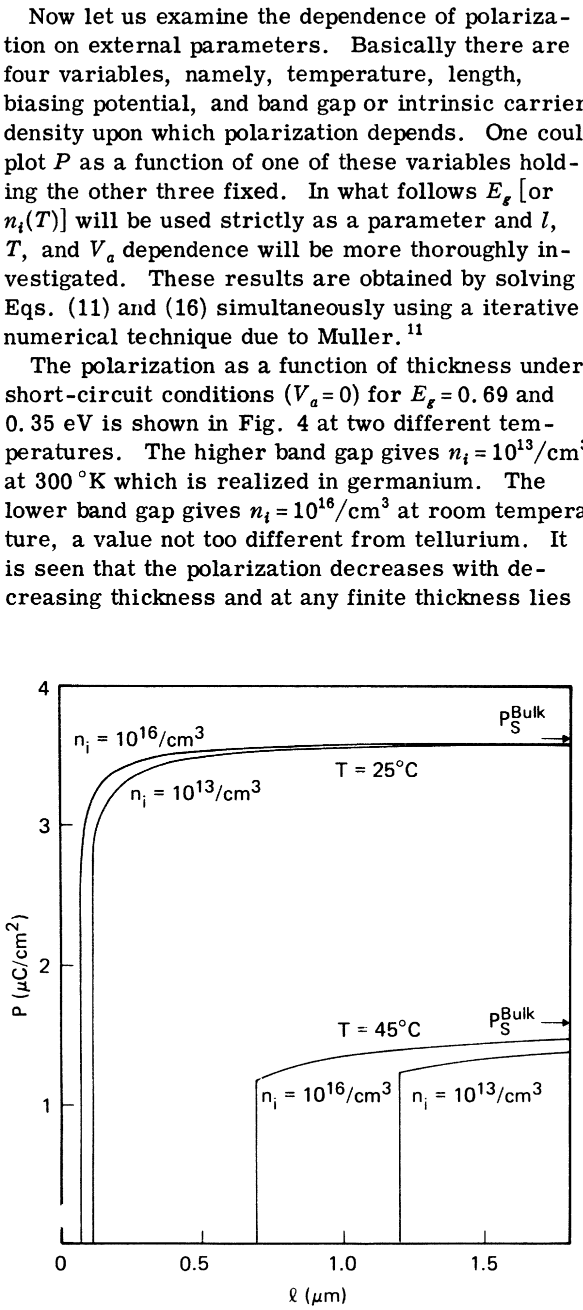

FIG. 4. Polarization P as a function of TGS film thickness l for different intrinsic carrier concentrations n_i in semiconducting electrodes.

The polarization as a function of temperature for $V_a = 0$ and $E_g = 0.69$ eV [$n_i(300\,^\circ\text{K}) = 10^{13}/\text{cm}^3$] for several values of l is shown in Fig. 5. The curve marked "Bulk" shows that the polarization goes continuously to zero at the transition temperature $T_0 = 49.8\,^\circ\text{C}$ showing a second-order transition for bulk TGS. At lower thicknesses of the ferroelectric film, the transition is of first order and takes place at a temperature T_c which is below T_0 and is l dependent. For a given l one can solve for T_c in a manner described for obtaining l_c at a given T. At any temperature above T_c, the free energy of the nonpolar state is lower than the free energy of the polar state and, consequently, a transition takes place at T_c. The transition temperature and the transition length play an equivalent role and may be used interchangeably in the physical description.

The shift in transition temperature $T_0 - T_c$ as a function of l is shown on a log-log plot in Fig. 6 for two different band gaps at $V_a = 0$. For higher-band-gap material (lower intrinsic carrier concentration) the shift is more than for the lower-band-gap material because of poorer compensation. Equivalently, Fig. 6 gives the temperature dependence of the transition length l_c. The thickness l_c at which the transition takes place is essentially proportional to $(T_0 - T)^{-3/2}$. This can be derived by eliminating P from the relations $F = 0$ [see Eq. (13)] and $\partial F/\partial P = 0$ [see Eq. (14)]. This T dependence can also be inferred by noting that the square-root dependence of P on $T_0 - T$ for bulk TGS is hardly changed in thin films (see Fig. 5) and, consequently, the first two terms in Eq. (14) are essentially proportional to $(T_0 - T)^{3/2}$. Since the last term in this equation is a weak function of T, $l_c \sim (T_0 - T)^{-3/2}$. This dependence has also been found[12] in superfluid thin films and could not be explained in terms of the usual Landau free-energy expansion.

The calculated polarization as a function of volt-

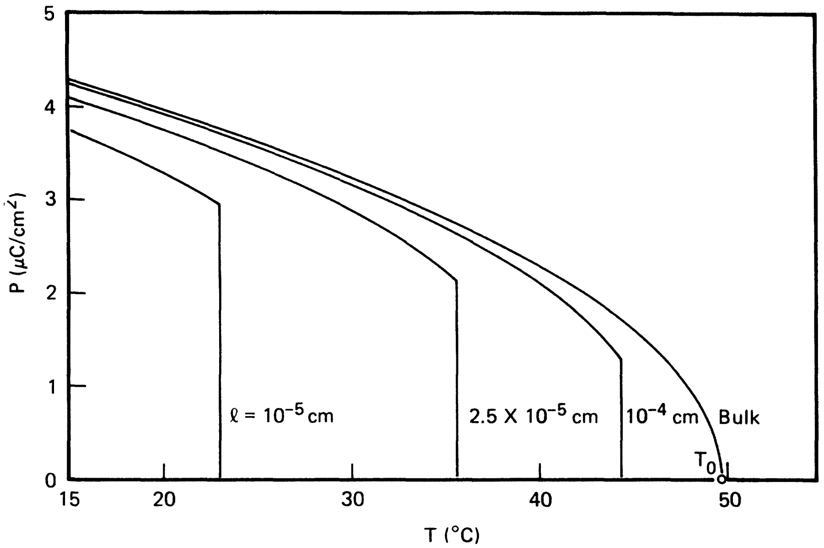

FIG. 5. Polarization P as a function of temperature T for different thicknesses of TGS films.

age is shown in Figs. 7 and 8. In Fig. 7 loops for different thicknesses but at the same temperature are shown, and in Fig. 8 thickness is held fixed for different temperatures. Both figures show double hysteresis loops which are characteristic for first-order transitions.[9] A TGS crystal of 100-μm thickness shows a normal loop and first-order double loops occur upon reducing the thickness, which also reduces the coercive field. In Fig. 8 double hysteresis loops result from an increase in temperature at constant thickness of the ferroelectric. One sees from these figures that an increase in temperature and reduction in thickness of the ferroelectric in a ferroelectric-semiconductor system have similar effects and lead to first-order transitions.

Now we are ready to examine the nature of the solutions. As mentioned earlier, upon simultaneously solving the nonlinear Eqs. (11) and (16), one ends up with several solutions belonging to polar and nonpolar states of the ferroelectric and to understand hysteresis loop, transition temperature, and transition length it is important to know which solutions are stable. This is conveniently done in terms of the stability plots[13] shown in Figs. 9 and 10, where different regions specify the type of solutions. Figure 9 gives the temperature dependence of polarization for $l = 10^{-5}$ cm and $E_g = 0.69$ eV for several values of applied voltage. The spontaneous bulk polarization is shown for comparison. The metastability limit which separates the region of absolutely stable polarization values from the metastable ones, and the stability limit which separates the metastable and unstable regions, are also drawn. The metastability limit is obtained through an iterative process which insures that in the presence of a field the free energy at the root "near" $P = 0$, which is a nonpolar solution (in the presence of a field P never exactly goes to zero), is equal to the free energy at the root in the polar state called the polar solution. In the absence of a field this process is rather straightforward because the free energy of the nonpolar state can be set equal to zero and this gives the metastability limit at T_c. Below this temperature, the metastability limit must coincide with the P curve corresponding to $V_a = 0$ because the free energy for the two polar solutions of opposite sign is equal and smaller than the free energy for the nonpolar solution. Any application of a field would make one or the other of the polar

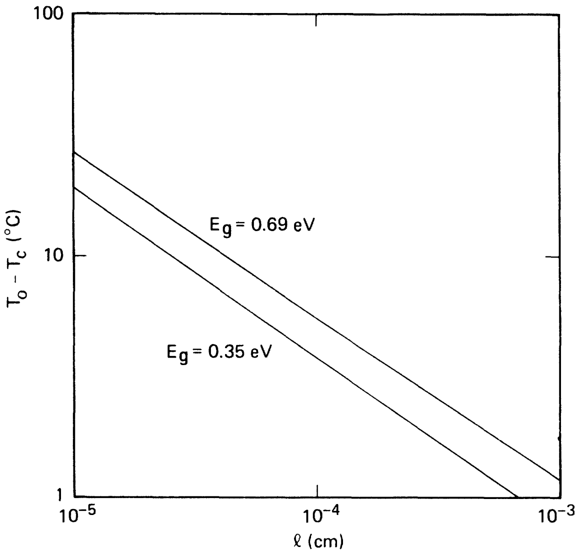

FIG. 6. Shift in transition temperature $T_0 - T_c$ of TGS films as a function of thickness l.

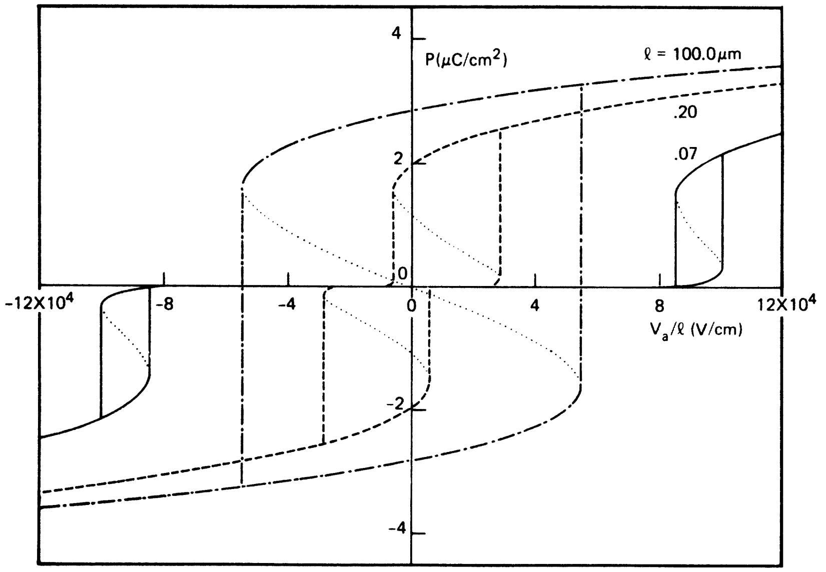

FIG. 7. Polarization P vs applied voltage V_a (hysteresis loops) for TGS films of different thickness at $T = 35\,^{\circ}\mathrm{C}$.

solutions absolutely stable. The stability limit is relatively easy to get because the solutions must also satisfy the condition $\partial^2 F/\partial P^2 = 0$ along with Eq. (16). One notes from Fig. 9 that for a given voltage at $T > T_c$, the P curve meets the metastability limit twice at different values of P but at the same temperature and intersects the stability limit at two different temperatures.

The transitions between different polarization states are a consequence of the intersection of the $P(T)$ curves with metastability and stability limits. Transitions occur from inside the metastable region to points in an absolutely stable region. As an example let us follow the polarization at an applied voltage of 0.65 V from low to high temperature in the upper-half of Fig. 9. The polarization is absolutely stable below 39 °C and becomes metastable at 39 °C and unstable at 39.7 °C which is the *superheating* temperature. The transition occurs somewhere between 39 and 39.7 °C. When we follow the same curve from high to low temperatures, the nonpolar state becomes metastable at 39 °C as did the polar state, but becomes unstable at the *supercooling* temperature of 33.8 °C. The transition may occur anywhere between 39 and 33.8 °C and it is of first order as indicated by the possibility of supercooling and superheating. Usually the transition temperature is defined at the metastabil-

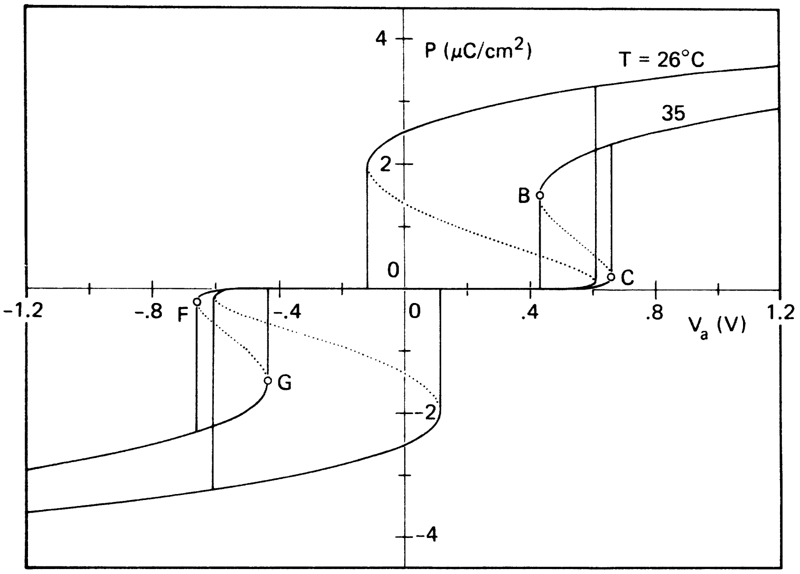

FIG. 8. Polarization P vs applied voltage V_a for a TGS film 10^{-5} cm thick at different temperatures.

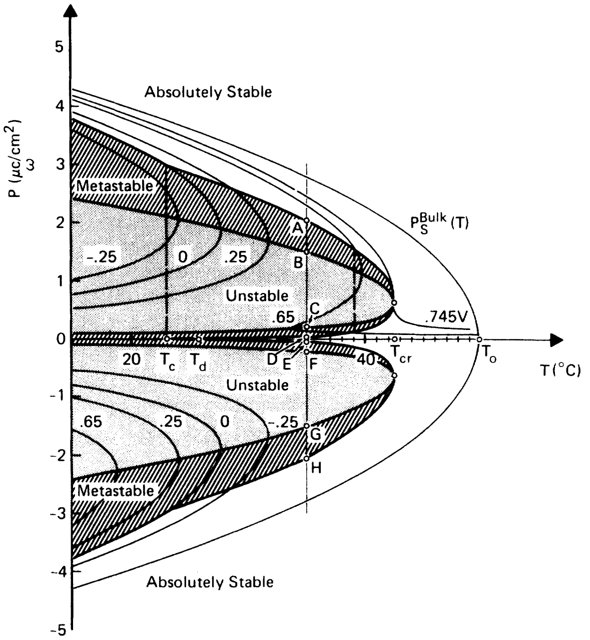

FIG. 9. Stability plot of a TGS film 10^{-5} cm thick with semiconducting electrodes of band gap $E_g = 0.69$ eV in the polarization-temperature plane.

ity limit. As is known,[8,13] a first-order transition will become a second-order transition in the presence of an applied voltage of proper magnitude. This occurs in Fig. 9 for the critical voltage $V_{cr} = 0.745$ V at the critical temperature $T_{cr} = 42.5$ °C. At higher voltages or at higher temperatures there is no phase transition. This is equivalent to the liquid-gas phase transition where these conclusions are drawn from a volume versus temperature plot.

Transitions at constant temperature as a function of voltage, i.e., the polarization versus voltage loop, can also be derived from Fig. 9. But a better way to do it is in conjunction with a voltage versus temperature plot given in Fig. 10 where the extensive variable (polarization P) has been exchanged by its conjugate intensive variable (voltage V_a). (While Fig. 9 resembles the volume versus temperature plot for gases, Fig. 10 corresponds to the pressure versus temperature plot.) The lines drawn in Fig. 10 give the voltage, as a function of temperature, which must be applied to bring the polarization on the stability or metastability limit. These lines separate regions of absolutely stable s, metastable m, and unstable u states. Since intersections of the $P(T)$ curve at constant voltage with the metastability limit in the upper-half of Fig. 9 occurred at the same temperature, the same voltage has to be assigned to the lower and upper branches of the metastability limit. Therefore both branches of the metastability limit are represented by a single line in Fig. 10, which begins at the critical point, meets the temperature axis at T_c, and follows it below T_c since for $T < T_c$ it is given by the zero-voltage curve in Fig. 9. Transitions as a function of temperature are usually taken to occur at the metastability limit and as a function of voltage at the stability limit. In general, however, actual transitions occur from a state somewhere in the metastable region to a state in an absolutely stable region.

To show the correspondence of the stability plots in Figs. 9 and 10, we will construct a polarization versus voltage loop at 35 °C as shown in Fig. 8. We begin at +0.7 V, where $P \gg 0$ is absolutely stable. Reducing the voltage, the polarization becomes metastable at A and unstable at B at a value of 1.5 μC/cm² as seen from Fig. 9 and at a voltage of +0.43 V as seen from Fig. 10. Also Fig. 10 shows that for $V_a \leq +0.43$ V, only $P \approx 0$ is absolutely stable. Therefore at +0.43 V, a transition occurs from $P = 1.5$ μC/cm² to $P \approx 0$. This solution remains absolutely stable until we reach point E where it becomes metastable. The transition, however, occurs at point F where $P \approx 0$ becomes unstable from $P = -0.2$ μC/cm² at a voltage of -0.66 V and it goes to an absolutely stable value of P

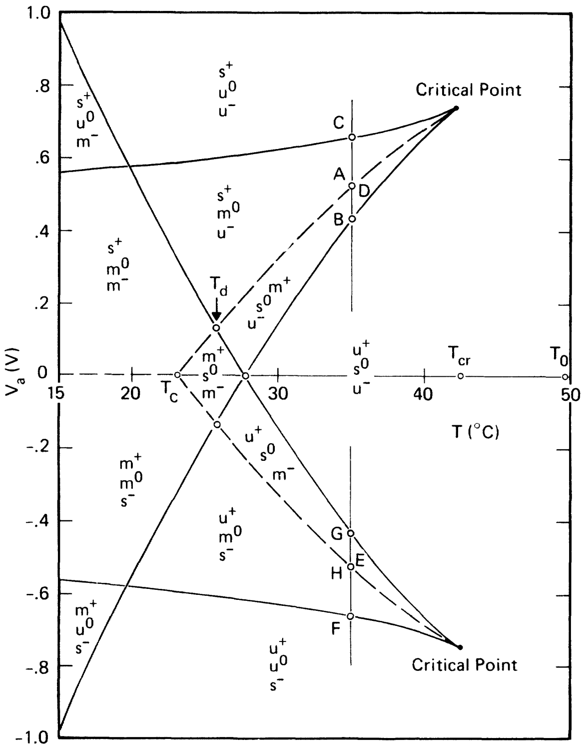

FIG. 10. Stability plot of a TGS film 10^{-5} cm thick with semiconducting electrodes of band gap $E_g = 0.69$ eV in the voltage-temperature plane. Superscripts +, 0, − identify regions where $P \gg 0$, $P \simeq 0$, and $P \ll 0$, respectively, are absolutely stable s, metastable m, or unstable u.

$< -2.1\ \mu C/cm^2$. Going back to a positive voltage, the transition from $P \ll 0$ to $P \approx 0$ occurs at point G and from $P \approx 0$ to $P \gg 0$ at point C, and this completes the double loop.

From Fig. 10 we see that below $T = T_d$ when one polar state becomes unstable the other is absolutely stable and the system does not make a transition to $P \simeq 0$. Consequently, the first-order character of the phase transition as a function of temperature manifests itself in double hysteresis loops only at $T > T_d$. Below T_d there are no double loops as the loop at 25 °C in Fig. 8 shows, although this is still above T_c.

The first-order behavior of the ferroelectric-semiconductor system as a function of temperature and voltage is revealed in the stability plots in Figs. 9 and 10, but since in our system the deviation from a second-order transition depends on the ferroelectric film thickness, the whole stability plot is "thickness dependent." With increasing thickness l of the ferroelectric, the transition temperature T_c at zero applied voltage approaches the critical temperature T_{cr} and both approach the bulk transition temperature T_0. As $T_{cr} \rightarrow T_0$, the polarization and voltage at the critical point tend to zero. The second-order transition occurs as the limiting case of the first-order transition for $l \rightarrow \infty$. Some indirect experimental verification of the predictions of the model has recently been presented[14] and further work is in progress.

IV. CONCLUSION

It is shown that a second-order bulk ferroelectric will exhibit a first-order transition when sandwiched between semiconducting electrodes. The change of the order of the phase transition is caused by the compensation charge distribution in the semiconducting electrodes. Furthermore, a thin ferroelectric film will show reduced values of polarization and transition temperature.

ACKNOWLEDGMENTS

One of us (P. W.) would like to thank the IBM Corp. for the opportunity to work at the San Jose Research Laboratory. Dr. E. Kay's continuing encouragement is sincerely appreciated. Useful discussions with Dr. G. Falk and Dr. W. Ruppel are gratefully acknowledged.

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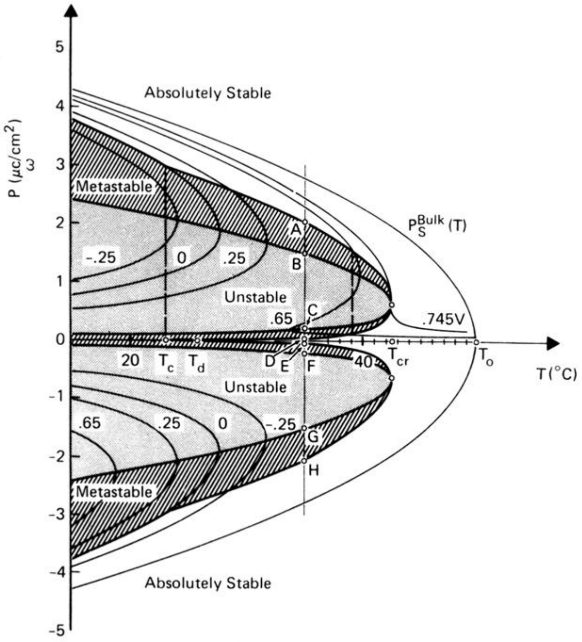

FIG. 9. Stability plot of a TGS film 10^{-5} cm thick with semiconducting electrodes of band gap $E_g = 0.69$ eV in the polarization-temperature plane.