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Depolarization-Field-Induced Instability in Thin Ferroelectric Films—Experiment and Theory

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The existence of depolarization fields in thin ferroelectric films is experimentally demonstrated by investigating an unconventional electrode-ferroelectric configuration consisting of a triglycine sulphate (TGS) film sandwiched between a gold and a doped-silicon electrode. Due to nonidentical electrodes, the compensating-charge distribution for opposite polarization directions is asymmetric and consequently depolarization fields cannot be sufficiently reduced by domain formation. These depolarization fields manifest themselves by reducing the intrinsic polarization in thin ferroelectric films with respect to the bulk value and this aspect is experimentally confirmed. For a sufficiently thin film, depolarization fields become too strong and a polarization instability is observed. These effects are simulated by altering the compensation-charge extension in the silicon electrode by photoillumination. Other causes, like impurities, and structural defects, which can lead to reduction of polarization, are ruled out. Theoretical model calculations including the depolarization field are reported. The calculation predicts an intrinsic polarization reduction in thin ferroelectric films and is in good agreement with experiments reported here.

I. INTRODUCTION

It has been widely discussed that cooperative phenomena should be size dependent since the cooperative interaction is weakened when it is restricted to dimensions less than or comparable to a coherence length. This idea has been much pursued in superconductivity with often contradictory results.[1] Besides observing a reduction of the cooperative interaction seen as a reduction of the transition temperature in thin films, an increase of the transition temperature as well as no dependence at all on sample thickness have also been reported. In superfluidity,[2,3] there is some experimental confirmation that the λ point in a film is lower than in a large volume of helium. In magnetism, no evidence for a thickness dependence of the spontaneous magnetization or transition temperature could be observed.[4] In ferroelectricity, surface layers with properties different from the bulk have been debated for a long time with no definite conclusions.[5]

Like superconductivity, where the cooperative interaction can be influenced by a magnetic field, the microscopic ferroelectric interaction is sensitive to macroscopic electric fields. But unlike superconductivity the ferroelectric polarization P itself is accompanied by an electric field if it is not completely compensated by charges in electrodes. This depolarization field is opposite to the polarization and tends to reduce it. It can be concluded that in ferroelectricity there are two different interactions, a microscopic interaction which tends to align dipoles and a macroscopic interaction via the depolarization field which tends to destroy this alignment. Both interactions have their own size dependence. The coherence length responsible for the size dependence of the microscopic interaction of dipoles is found[6] to be very small and thus cannot account for many experimental observations.

In this work we will investigate depolarization effects which are caused by incomplete compensation of the polarization in a ferroelectric film of thickness l. Without compensation the depolarization field is $4\pi P$, which for usual values of polarization of 1 μC/cm^2 is 10^7 V/cm. For depolarization fields $\gtrsim 10^5$ V/cm, however, the polarization is thermodynamically unstable. We see that for stable polarization values there has to be a very close compensation and therefore electrode properties are very important. It has been realized[7] that for thin ferroelectric films there will always be a lack of compensation. This is illustrated for a ferroelectric film sandwiched between a metal and a doped-semiconductor electrode of equal work function ϕ in Fig. 1. This unconventional configuration is chosen because we believe that the domain formation cannot eliminate depolarization fields in such a system. This point will be explained more fully later. The accomodation of the compensation charge results in bending the conduction band E_c and the valence band E_v. Because of the high carrier density there is only a slight bending of the bands in the metal electrode which can be neglected. The electrostatic potential V is drawn parallel to the bands but is displaced from them by the electron affinity χ (see Fig. 1). The band bending qV_b (since the bending in the metallic electrode is neglected) gives rise to a depolarization field in the ferroelectric which under short-circuit conditions is given by the band bending divided by the thickness of the ferroelectric. In thin ferroelectric films therefore the depolarization field can become very strong. Reduction of polarization values and transition temperature has been predicted for thin films and, depending on the distribution of the

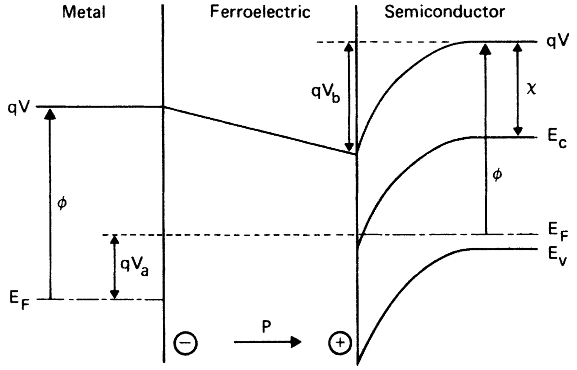

FIG. 1. Distribution of potential V in a ferroelectric thin film sandwiched between a metal and a semiconducting electrode for an applied bias V_a.

compensation charge in the electrodes, even a change of the order of the phase transition may result.[8]

A thickness dependence of the polarization has previously been reported for $BaTiO_3$ single crystals with metal electrodes.[9] It is, however, not clear to what extent the decrease of polarization by reducing the thickness is caused by structural defects, impurities, and formation of domains, since under usual conditions depolarization fields in a ferroelectric can be avoided by the formation of domains. The reduction of the polarization seen in experiments is in most cases caused by an arrangement of domains with opposite polarization directions while the intrinsic polarization inside a domain is not reduced. It has been proposed recently by Wurfel, Batra, and Jacobs[10] that these difficulties can be avoided in an asymmetric structure consisting of a triglycine sulphate (TGS) thin film deposited on a silicon substrate with gold as second electrode. As can be seen from Fig. 1, a change of the band bending V_b in the electrodes is equivalent to a change of the thickness of the ferroelectric because both change the depolarization field. Instead of changing the depolarization conditions by varying the thickness of the ferroelectric we will change the band bending in the semiconducting electrode, which can readily be done by illumination; thereby the behavior of the ferroelectric under different depolarization conditions can be examined in one and the same sample ruling out the influence of structural defects and impurities. Furthermore, the asymmetry of the Au-TGS-Si configuration does not allow the cancellation of depolarization fields by the formation of domains as will be discussed later. In a recent letter[10] it was shown that due to depolarization fields the polarization in an Au-TGS-Si structure was completely unstable. The purpose of this work is to present further experimental results which prove the existence of depolarization fields in thin ferroelectric films. Model calculations which include depolarization fields are also presented. It is shown that these calculations adequately account for the experimental findings here. In Sec. II we present the experimental results and the theory is discussed in Sec. III.

II. EXPERIMENT

Thin films of TGS were deposited on single-crystal-silicon wafers as described elsewhere[11] and a Au contact was evaporated as second electrode. Polarization-versus-voltage loops were measured using a modified Sawyer-Tower circuit[12] shown in Fig. 2. The electrometer E was introduced to provide a dc coupling between the capacitor C and the oscilloscope. This makes it possible to determine if opposite polarization directions are differently affected by the illumination of the semiconducting electrode. Figure 3 shows two loops taken at 25 °C and 100 Hz in a TGS thin film ~ 1-μm thick on a p-type Si substrate with 10^{15} acceptors/cm^3. The applied voltage V_a is given with reference to the Au electrode. Positive polarization in Fig. 3 means that the polarization vector is directed towards the Si electrode requiring negative charge for compensation which has to be provided by accumulation of minority carriers (electrons) at the interface (if possible) and by depletion of majority carriers. Negative polarization values in Fig. 3 require positive charge for compensation in the Si electrode which is provided by majority-carrier accumulation.

The small loop in Fig. 3 is taken in the dark and the fully saturated loop is observed under high-intensity illumination. Since under illumination of the Si electrode a high carrier density becomes available for compensation of the polarization, the Si electrode behaves more like a metal, the depolarization field present in the dark disappears, and the polarization becomes fully saturated. By comparing the loops in the dark and under illumination

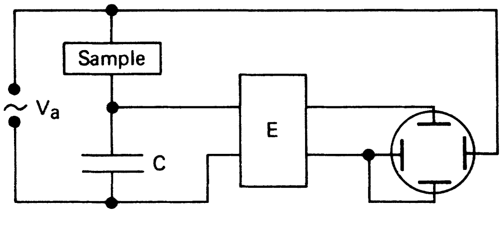

FIG. 2. Sawyer-Tower circuit modified by electrometer E to give dc coupling between capacitor C and oscilloscope.

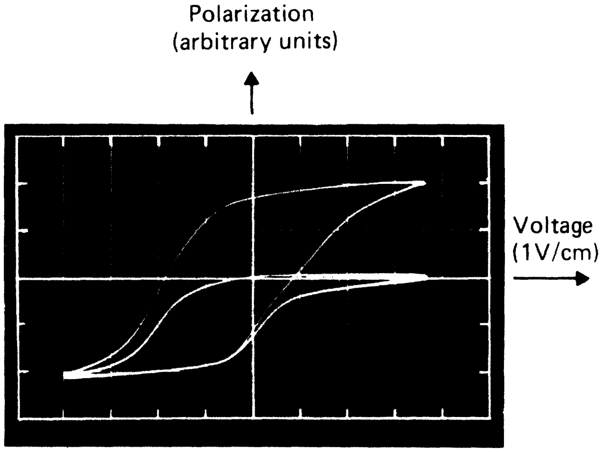

FIG. 3. Polarization-vs-voltage loop at 100 Hz in a TGS film ~ 1-μm thick between a Au and a p-type Si electrode with 10^{15} acceptors/cm^3. The small loop is taken in the dark, the saturated loop under illumination after heating the sample above the Curie temperature of 50 °C and cooling it to room temperature quickly.

we see the effect of the depolarization field alone with no contributions from impurities and structural defects. We note in Fig. 3 that negative polarization values are not altered by the illumination. Obviously majority-carrier accumulation by which negative polarization values are compensated does not lead to a sizeable band bending since that would change under illumination. Positive polarization values, however, are totally unstable in the dark due to high depolarization fields caused by very large band bending associated with majority-carrier depletion. The accumulation of minority carriers can be neglected in the dark at frequencies > 1 Hz because their thermal generation is a very slow process.[13]

The loops in Fig. 3 were obtained after keeping the sample for several minutes above the Curie temperature of 50 °C and cooling it down to room temperature quickly. By this process majority carriers which were trapped in slow interface states during their accumulation in every cycle are released from the interface. When we keep the sample at room temperature the loops change to the ones shown in Fig. 4. The loop in the dark now does not even reach zero polarization indicating the influence of a trapped charge of majority carriers which is almost constant during a cycle. This charge is located in interface states which are present with densities on the order of 10^{14}/cm^2 eV as was determined by photovoltage measurements. The interface charge almost compensates saturated negative polarization values and explains why there is no band bending associated with negative polarization values. When at positive voltages the negative polarization decreases in magnitude and becomes less than this trapped sheet charge, an electric field opposite to the applied voltage is caused in the ferroelectric which keeps the polarization at negative values. In this case the trapped sheet charge is a little larger than the polarization and has to be compensated by majority-carrier depletion in the adjacent Si. Depletion therefore occurs even when the polarization is still negative.

When minority carriers are generated at a rate higher than the thermal rate by illumination, the compensation improves, positive polarization values become stable, and at high illumination intensities we observe a saturated loop. The instability of polarization values which require depletion of majority carriers could only be demonstrated by comparison with saturated loops taken in the same sample so that all other causes for a decrease of the polarization, like structural defects and impurities, are eliminated. The illumination was synchronized to the voltage applied to the sample by means of a light chopper in such a way that two subsequent loops were always taken in the dark and every third loop under illumination. It is also ensured that the loops are not altered by resistance effects since the RC time constant for supplying the compensation charge is $< 10^{-5}$ sec.

Minority carriers have been neglected at 100 Hz in the dark because their thermal generation is too slow, but we expect that their contribution to the total compensation charge becomes important when the loops are traced at lower frequencies, which will improve the compensation and lower the depolarization field so that positive polarization values become stable. It can be presumed that during majority-carrier depletion minority carriers are

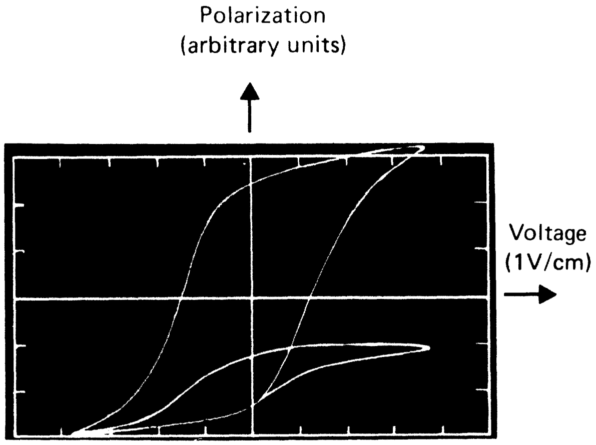

FIG. 4. Same as in Fig. 3 but after keeping the sample for 1 h at room temperature.

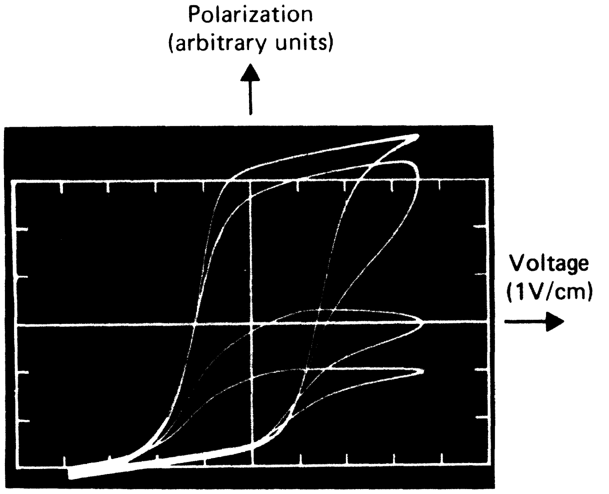

FIG. 5. Loops traced in the dark at different frequencies. The smallest loop is taken at 100 Hz the largest at 0.1 Hz with loops at 10 and 1 Hz in between.

driven to the interface by the field in the space charge region of the Si and are trapped in interface states. A minority-carrier sheet charge builds up at a rate proportional to the minority-carrier generation. When there is sufficient time during every loop to build up a minority-carrier sheet charge which can compensate entirely the polarization and the trapped majority-carrier charge, the depolarization field will disappear and positive polarization values will be saturated too. This is demonstrated by the loops shown in Fig. 5 which were traced in the dark at different frequencies. With decreasing frequency the time available for building up the minority-carrier charge increases and the compensation improves until at 0.1 Hz a saturated loop is observed.

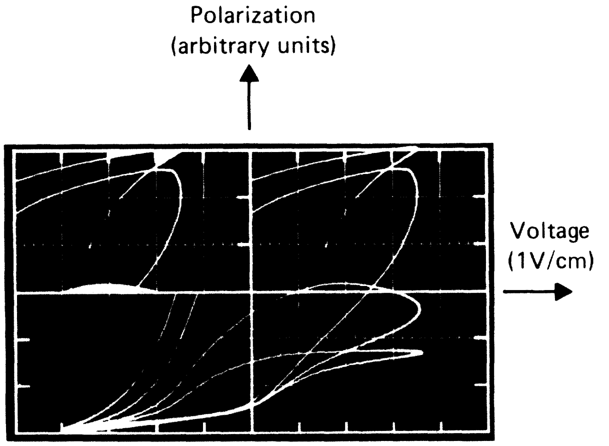

FIG. 6. Loops traced at 100 Hz at different illumination levels. The smallest loop is taken in the dark, the saturated loop at the highest intensity.

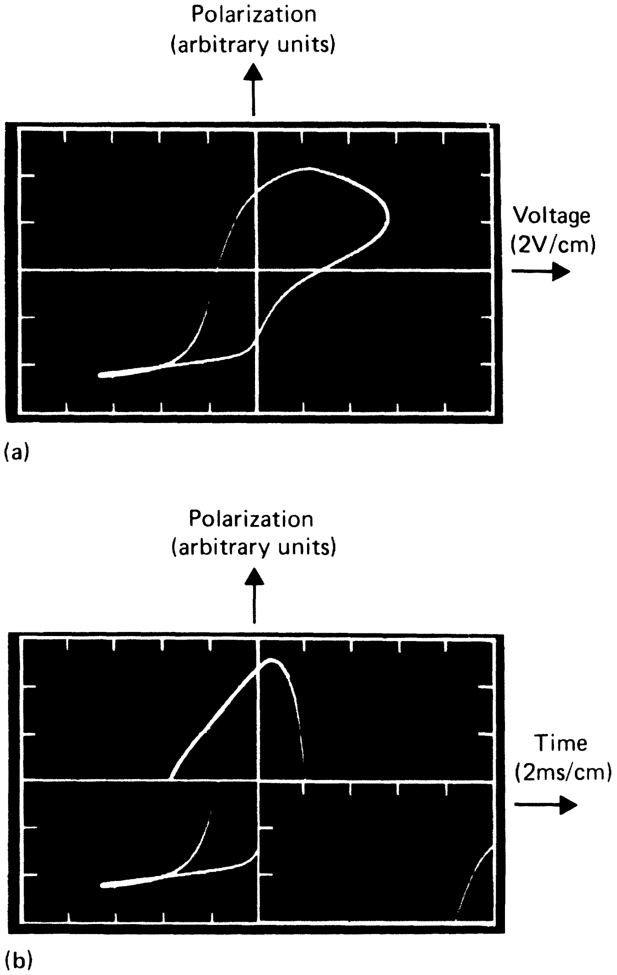

FIG. 7. (a) Polarization vs voltage at medium illumination intensity; (b) polarization vs time at the same intensity.

We can demonstrate the effect of minority-carrier generation also by keeping the time available for building up the minority-carrier charge constant and varying instead the minority-carrier generation rate by illuminating the sample. The result is shown in Fig. 6. The loops taken at the constant frequency of 100 Hz but at different illumination intensities are very similar to the loops in Fig. 5 taken in the dark but at different frequencies.

The rather strange shape of the polarization-versus-voltage loop at intermediate illumination levels [Fig. 7(a)] finds a very simple explanation when the polarization during a loop is shown as a function of time [Fig. 7(b)]. Since it is known that the polarization can never differ very much from the compensation charge, we see that a linear increase of the accumulated minority-carrier charge caused by a constant generation rate is responsible for the strange shape of the loops. The idea that the polarization is controlled by the accumulated minority carriers is further confirmed in Fig. 8, where the slope γ of the linear increase of the $P(t)$ curve shows a linear dependence on illumination intensity. We have plotted the inverse because at infinite intensity the slope is governed by intrinsic parameters of the ferroelectric and does not become infinite. The filled circles in Fig. 8 are experimental points which lie on a straight line.

For n-type Si substrates, where holes are the minority carriers, a polarization pointing away from the Si substrate should lead to a depletion of majority carriers and we expect negative polarization values to be suppressed. This is indeed the case as shown in Fig. 9. Since this n-type Si substrate was doped with 10^{17} donors/cm^3, there was better compensation possible and the polarization is not as severely reduced as it was in Fig. 3 where the doping concentration was 10^{15}.

We have now determined that a depolarization field in a metal-ferroelectric-semiconductor structure is caused by the depletion of majority carriers and that it decreases when minority carriers are generated either thermally or by external excitation. It was also shown that the value of the polarization is reduced in the presence of this depolarization field. These concepts are developed more fully in Sec. III.

III. MODEL CALCULATIONS

We will now theoretically derive polarization-versus-voltage loops and verify the depolarization field concept by comparison with experiments. We will first determine thermodynamic stable values of the polarization in a unidomain TGS thin ferroelectric film from free-energy considerations. Although the TGS films which we used were not single crystalline and therefore not unidomain, the thermodynamic calculation will give us limits of polarization values and the experimentally observed values have to be within these limits. The calculation will be done using the same parameters as in the experimental loops in Fig. 6, where at a constant frequency of 100 Hz the illumination was changed from zero to high intensity.

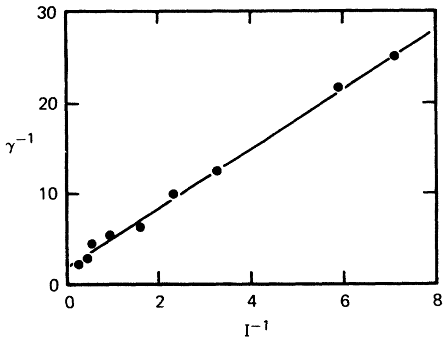

FIG. 8. Inverse slope γ^{-1} of the linear part in the $P(t)$ curve Fig. 7(b) as a function of inverse intensity I^{-1}.

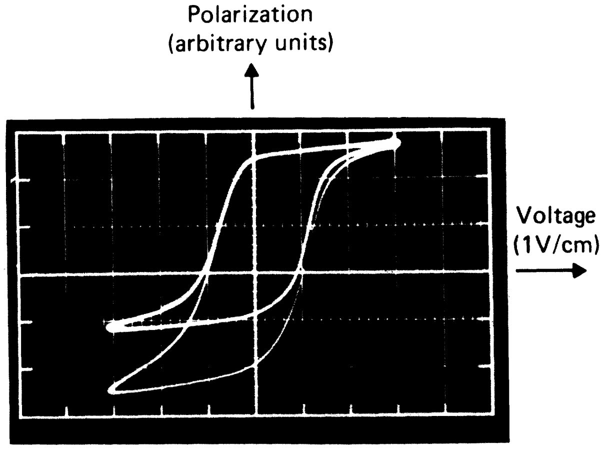

FIG. 9. Loop at 100 Hz in a TGS film ~ 1-μm thick on an n-type Si substrate with 10^{17} donors/cm^3.

The free energy of a second-order ferroelectric like TGS sandwiched between a metal and a semiconducting electrode is

$$F = F_0 + \tfrac{1}{2}aP^2 + \tfrac{1}{4}\xi P^4 - \int_0^P E_f\, dp + \frac{\epsilon}{8\pi l}\int_0^\infty E_e^2\, dx \,, \qquad (1)$$

where F_0 is the free energy of the nonpolar phase which we set equal to zero for convenience. ξ and $a\,[\equiv 4\pi(T-T_0)/C]$ are the usual expansion coefficients with the Curie temperature T_0 and the Curie constant C. The last term in Eq. (1) takes into account that there is electrostatic energy associated with the spatial distribution of the compensation charge in the electrode. E_e is the electric field in the electrode. The field E_f in the ferroelectric follows from Fig. 1 and is

$$E_f = (1/l)(V_a - V_b) \,, \qquad (2)$$

where l is the thickness of the ferroelectric. $V_a = V_{a_0}\sin(\omega t)$ is the applied voltage and V_b is the band bending in the Si electrode, which we take as p type, doped with 10^{15} acceptors/cm^3. For majority-carrier depletion, V_b is related to the total charge ρ_s in the space charge region and can be easily shown to be given by[14]

$$V_b = 2\pi\rho_s^2/\epsilon q N_A \,, \qquad (3)$$

where $\epsilon = 6$ is the dielectric constant for Si, q is the magnitude of the electronic charge, and N_A is the acceptor density in the Si electrode. The field E_f in the ferroelectric is

$$E_f = (1/l)(V_a - 2\pi\rho_s^2/\epsilon q N_A) \ . \tag{4}$$

For majority-carrier accumulation the band bending is neglected and we develop the theory for majority-carrier depletion only. When the Si electrode is illuminated, minority carriers are generated and they are driven to the interface by the field in the depletion region. The total charge in the semiconducting electrode which is available for compensation is thereby increased. If we assume that all minority carriers which are generated within a diffusion length L_D of the interface reach the interface, then the accumulated charge due to the generation of minority carriers is

$$\rho_M = -qgL_D(t - t_0), \quad t > t_0 \ .$$

A constant generation rate g is assumed and t_0 is the time when the charge distribution in the electrode changes from accumulation to depletion of majority carriers due to a change in the polarization. When we also take into account that majority carriers are trapped in slow interface states which leads to a time-independent sheet charge Q_T then the total charge ρ_0 in the semiconducting electrode becomes

$$\rho_0 = Q_T - qgL_D(t - t_0) - \rho_s \ . \tag{5}$$

From the continuity of the dielectric displacement vector at the interface we also find

$$E_f = 4\pi(P + \rho_0) \ , \tag{6}$$

and by combining Eqs. (4)–(6) we get a relation between the polarization and the compensating charges

$$P = \frac{V_a}{4\pi l} - \frac{\rho_s^2}{2\epsilon q N_A l} - Q_T + qgL_D(t - t_0) + \rho_s \ . \tag{7}$$

The electric field E_e in the electrode is[14]

$$E_e = -(4\pi q N_A/\epsilon)(x - x_0) \ , \tag{8}$$

where x_0 is the width of the space charge region which is related to the charge ρ_s by $x_0 = \rho_s/qN_A$. The electrostatic energy in the electrode then becomes

$$\frac{\epsilon}{8\pi l}\int_0^{x_0} E_e^2 \, dx = \frac{2\pi\rho_s^3}{3\epsilon q N_A l} . \tag{9}$$

Equilibrium values of polarization are calculated at the minimum of the free energy and therefore we need the first two derivatives with respect to P. Using Eqs. (1), (4), (7), and (9) we find

$$\frac{\partial F}{\partial P} = aP + \xi P^3 + \frac{2\pi\rho_s^2}{\epsilon q N_A l}(1 + \delta) - \frac{V_a}{l} \tag{10}$$

and

$$\frac{\partial^2 F}{\partial P^2} = a + 3\xi P^2 + \frac{2\pi\rho_s\delta}{\epsilon q N_A l}\left[2 + \left(2 - \frac{\rho_s\delta}{\epsilon q N_A l}\right)\delta\right] \ , \tag{11}$$

where

$$\delta \equiv \frac{1}{\rho_s/\epsilon q N_A l + 1} \ .$$

Stable equilibrium values of polarization have to satisfy the conditions

$$\frac{\partial F}{\partial P} = 0 \tag{12}$$

and

$$\frac{\partial^2 F}{\partial P^2} > 0 \ . \tag{13}$$

When the stability limit $\partial^2 F/\partial P^2 = 0$ is reached a transition must occur. In a polydomain ferroelectric the transition occurs in general in the metastability region far from the limit of stability but the saturated polarization value to which the transition occurs follows from Eqs. (12) and (13), i.e., from the thermodynamic calculation.

Polarization-versus-voltage loops were calculated from Eqs. (7) and (12) for several minority-carrier generation rates. Best agreement with the experimental results shown in Fig. 6 was obtained when the magnitude of the trapped majority-carrier charge Q_T was set equal to $\frac{3}{4}P_s$, where P_s is the spontaneous bulk polarization value. The calculated thermodynamic equilibrium values of polarization at one illumination level are shown in Fig. 10 by the full curve. Starting with $P < 0$ from $V_a = 0$ to $V_a > 0$, there is only one stable solution for the polarization. With increasing voltage V_a and increasing accumulation of minority carriers at the interface the compensation improves and at point B two more solutions appear. To decide which one of them is stable the stability limit has been calculated from the condition $\partial^2 F/\partial P^2 = 0$ and is given by the dashed lines in Fig. 10. The stability limit starts at point A. Stable polarization values have to be either below the lower branch or above the upper branch of the stability limit. This indicates that of the two solutions which emerge at point B, the rapidly rising solution is stable and the other one is unstable. The upper branch of the stability limit then saturates at about $+2.1$ μC/cm^2 and $P > 0$ (the stable solution) reaches a maximum value when the voltage V_a is already decreasing. From this point on the accumulated minority-carrier charge completely neutralizes the polarization and the depolarization field has been eliminated. This calculation shows that there is a stable positive solution which grows proportional to the accumulation of minority carriers. However, starting with $P < 0$ this unidomain calculation does not predict a transition to $P > 0$ for the range of voltage used ex-

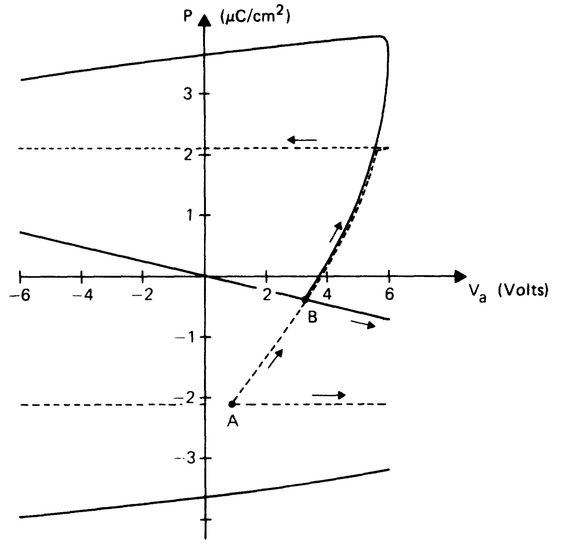

FIG. 10. Thermodynamic equilibrium values of polarization in a unidomain TGS thin film on a p-type Si substrate (full curve) and thermodynamic stability limit (dashed curves).

perimentally, because the equilibrium values $P < 0$ do not meet the lower branch of the stability limit. The transition which is observed experimentally must therefore have another origin and it is well known that in all ferroelectrics the transition from $P < 0$ to $P > 0$ occurs by the formation of domains and by the movement of domain walls and cannot be described by a thermodynamic unidomain calculation.[15]

To provide for transition between the thermodynamically stable solutions $P < 0$ and $P > 0$ we have calculated the switching process due to domain movement. In the switching theory the rate of change of the average polarization $\overline{P}$ is given by

$$\frac{d\overline{P}}{dt} = [P(E_f) - \overline{P}]\,\nu\, e^{-\alpha/E_f} . \qquad (14)$$

The factor $[P(E_f) - \overline{P}]$ is proportional to the area of unswitched domains. $P(E_f)$ is the thermodynamically stable polarization inside the domains which expand due to the field E_f in the ferroelectric, and follows from Eqs. (7) and (12). The factor $[P(E_f) - \overline{P}]$ ensures that the average polarization $\overline{P}$ saturates when it reaches the value of the intrinsic polarization $P(E_f)$. The constant ν is taken to be 10^8 Hz and the activation field α for the movement of domain walls is set equal to 300 esu. The values of these constants are, however, not critical for our results.

For the switching calculation we make use of the fact that for stable polarization values $P \approx -\rho_0$ and substituting the space charge ρ_s from Eq. (5) into Eq. (4) we find

$$E_f = \frac{V_a(t)}{l} - \frac{2\pi}{\epsilon q N_A l}\left[Q_T + P - qgL_D(t - t_0)\right]^2 . \qquad (15)$$

With the field given in Eq. (15) we can now calculate the polarization as a function of applied voltage from Eq. (14). Hysteresis loops for several different illumination intensities characterized by the parameter Rate $\equiv qgL_D$ are shown in Fig. 11. The switching model now gives transitions from thermodynamically metastable polarization values to absolutely stable values. By comparison with the result of the thermodynamic calculation we see that the transition region is rather small and the thermodynamically stable maximum polarization is reached fast. In the experimental loops the transition region is broader, the transitions are less steep. The agreement between theory and experiment is good except that the theory predicts an increase of the polarization as long as the field in the ferroelectric is parallel to the polarization. The experiment, however, seems to indicate that the polarization itself depends on the magnitude of the field strength in the ferroelectric. It decreases when the field decreases. This is not surprising since the ferroelectric TGS films have structural imperfections which lead to a higher polarizability or dielectric constant than the theory based on perfect single crystals can predict.

The application of this simple theory which leads

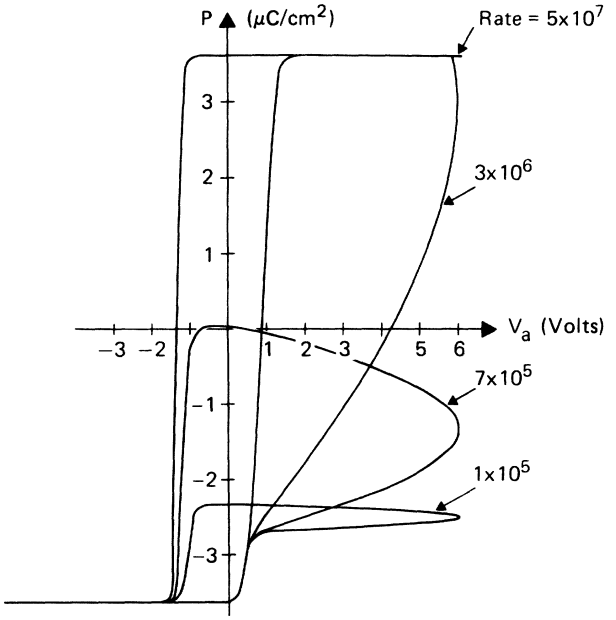

FIG. 11. Loops calculated from a combination of switching theory and thermodynamic theory for the same parameters as for the experimental curves shown in Fig. 6. The parameter Rate $\equiv qgL_D$ (see text for explanation of symbols).

to good agreement with experimental results is, however, only possible for the asymmetric structure which we used. In a symmetric structure depolarization fields can be avoided by the formation of domains because opposite polarization directions are equally accompanied by depolarization fields. These fields cancel at the boundary of domains with opposite polarization direction and when the domains are small enough the depolarization fields cancel all over. The polarization in each domain then has its saturated value and is not reduced due to depolarization effects as the thermodynamic theory would predict in the unidomain case. In our structure the negative polarization direction is not accompanied by a depolarization field since in this direction the polarization is well compensated by majority-carrier accumulation.[10] Only the positive polarization direction which leads to majority-carrier depletion in the Si electrode is insufficiently compensated and therefore accompanied by a depolarization field. Because of this property of our structure the depolarization field cannot be eliminated by the formation of domains. Therefore, the polarization inside each domain has to be calculated from the thermodynamic theory in the presence of the depolarization field. Since this leads to a good agreement with experiments we are convinced that the experimentally observed zero value of polarization in Fig. 4 is the thermodynamic unidomain value that means the domains are parallel to each other in all crystallites of the film and that we, for the first time, have seen the intrinsic reduction of the polarization in thin films due to depolarization effects.

IV. SUMMARY

We have shown experimentally that the compensation of the polarization is incomplete in thin ferroelectric TGS films. This leads to severe reductions of the polarization, when the thickness of the ferroelectric becomes comparable to the extension of the compensating charge in the electrodes. By using a semiconducting electrode where this extension is large and can be modified by photoillumination the dependence of the polarization on depolarization conditions could clearly be demonstrated and the effect of structural defects and impurities is ruled out. Also, due to the asymmetry, domain formation cannot eliminate the depolarization effect, and the polarization is reduced intrinsically. It has recently been proposed[8] that a TGS thin film with semiconducting contacts should exhibit a first-order phase transition. This prediction is, however, not applicable to our experiments since it requires the minority carriers to be in thermal equilibrium which is not the case in our measurements. The theoretical analysis presented here also shows that under the present circumstances the phase transition remains of second order. Our observation of the instability of the polarization in a ferroelectric semiconductor sandwich reveals severe limitations to the feasability of ferroelectric-semiconductor devices.[17]

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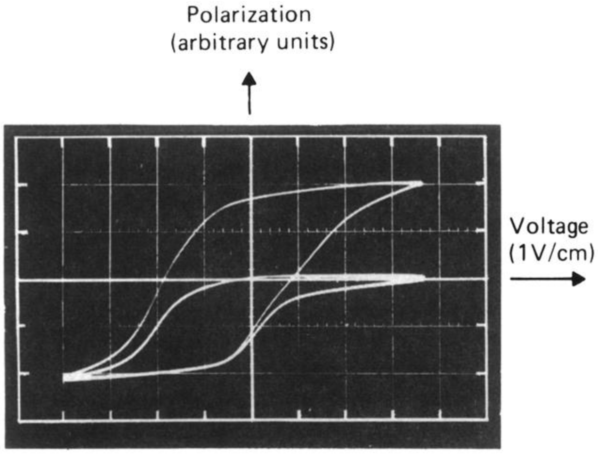

FIG. 3. Polarization-vs-voltage loop at 100 Hz in a TGS film ~ 1-μm thick between a Au and a p-type Si electrode with 10^{15} acceptors/cm^3. The small loop is taken in the dark, the saturated loop under illumination after heating the sample above the Curie temperature of 50 °C and cooling it to room temperature quickly.

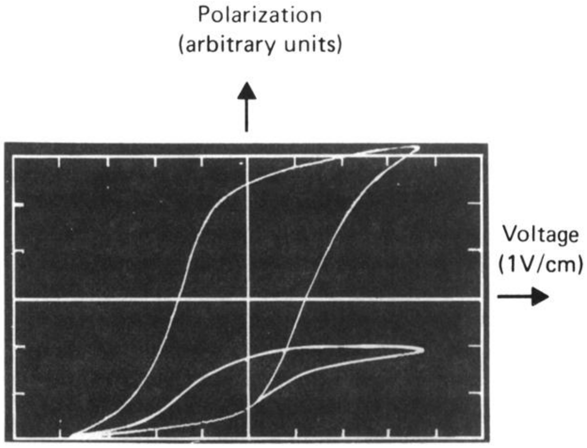

FIG. 4. Same as in Fig. 3 but after keeping the sample for 1 h at room temperature.

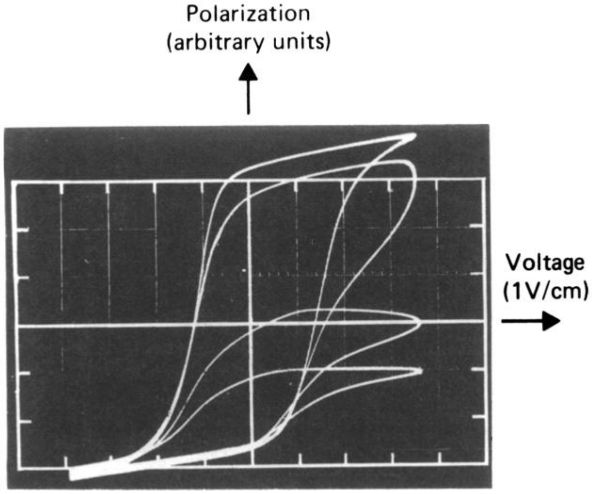

FIG. 5. Loops traced in the dark at different frequencies. The smallest loop is taken at 100 Hz the largest at 0.1 Hz with loops at 10 and 1 Hz in between.

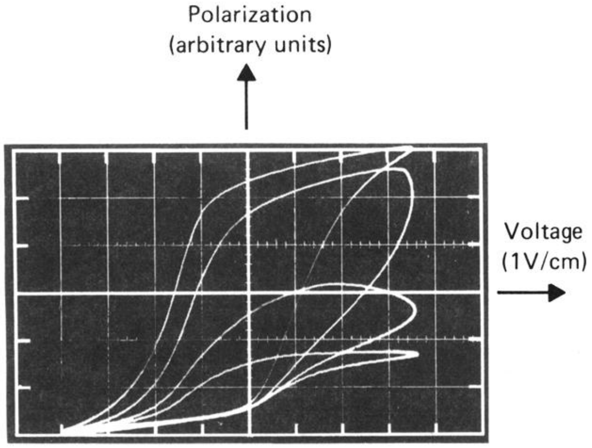

FIG. 6. Loops traced at 100 Hz at different illumination levels. The smallest loop is taken in the dark, the saturated loop at the highest intensity.

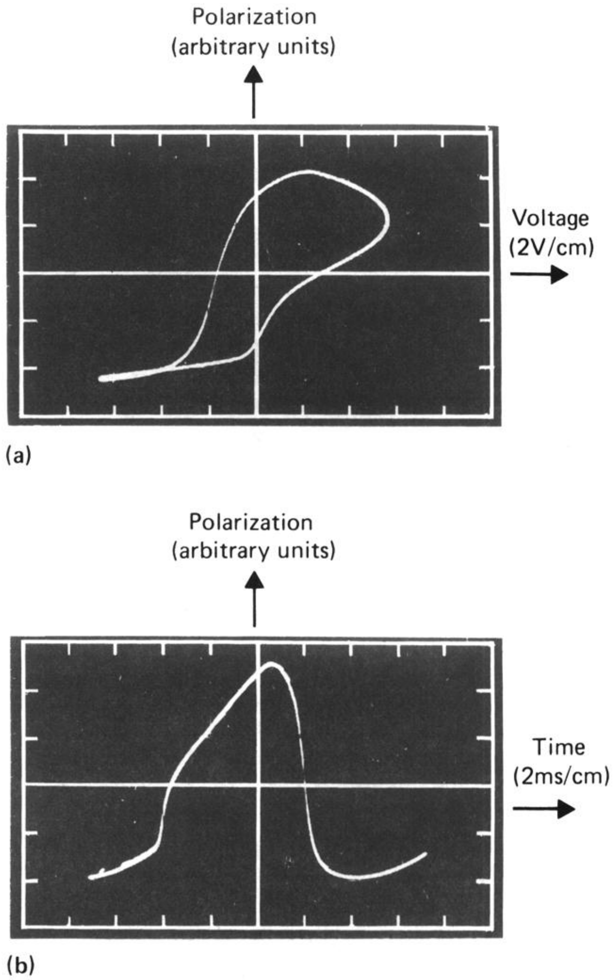

FIG. 7. (a) Polarization vs voltage at medium illumination intensity; (b) polarization vs time at the same intensity.

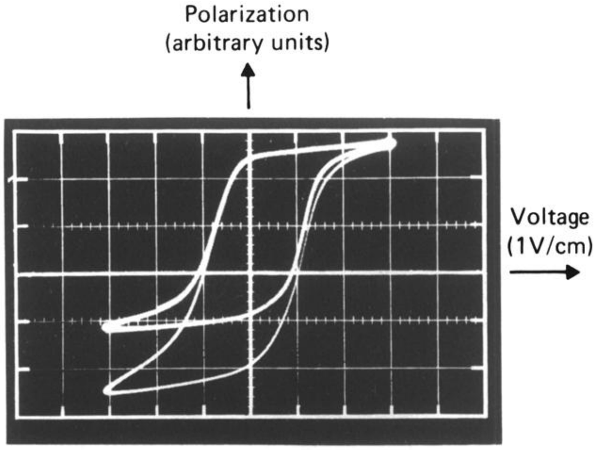

FIG. 9. Loop at 100 Hz in a TGS film ~1-μm thick on an *n*-type Si substrate with 10^{17} donors/cm^3.