Polarization Instability in Thin Ferroelectric Films

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(Received 18 May 1973)

An experimental study of critical phenomena in thin ferroelectric films is presented which, for the first time, conclusively demonstrates that the polarization in thin films is drastically reduced as a result of depolarization effects. Other causes, like impurities, structural defects, and domain formation, which can lead to reduction of polarization, are ruled out.

In recent years there has been active interest in cooperative phenomena in thin films. The dependence of transition temperature on film dimension has been extensively studied in superconductivity and to a lesser extent in superfluidity, ferromagnetism, and ferroelectricity. The critical properties of thin films are significantly different from the bulk properties, and these size effects become prominent when a characteristic coherence distance of the physical system becomes comparable with the sample thickness. With recent developments[1,2] in the area of superconductivity there seems to be adequate understanding of the experimental size dependence of the transition temperature. In superfluidity[2,3] there is also some experimental confirmation that the λ point in the film is lower than in the case of large volumes of helium. In ferromagnetism[4] this issue has been debated but there is no evidence that the transition temperature is different in thin films. Lately, there has been much discussion[5,6] of similar effects in ferroelectrics. Although there is some experimental evidence for a thickness dependence of the magnitude of the polarization,[7] it is not clear to what extent this is caused by domain formation, or by impurities and structural defects usually present in thin films and crystals.[8] The purpose of this communication is to present an experimental study of polarization reduction in thin ferroelectric films. The influence of domain formation, impurities, and structural defects is ruled out. For the first time it is conclusively demonstrated that the polarization in thin ferroelectric films is severely modified when the film thickness is comparable to the space-charge region in the electrode over which the compensating charge extends.

It has been shown theoretically[5] that in a thin ferroelectric film sandwiched between two semiconducting electrodes under short-circuit conditions the compensation of polarization is incomplete. Associated with it is a depolarization field in the ferroelectric opposite to the polarization which leads to reduction in polarization values and depression of transition temperature in thin films when compared with the bulk value. Since the details of charge compensation are important, the properties of a ferroelectric depend on its thickness and on the nature of the electrodes. It has been predicted[5] that with increasing thickness of the ferroelectric or higher space-charge densities in the electrodes, the compensation of the polarization is improved and its magnitude is closer to the spontaneous bulk polarization. However, even with metallic electrodes, there is always a critical thickness of the ferroelectric below which it does not exhibit any polarization. These considerations are valid for a unidomain ferroelectric. No experimental confirmation of these findings has yet been reported because under usual conditions the ferroelectric can avoid high depolarization fields by breaking up into domains. The average polarization which is experimentally observed is thus reduced but the intrinsic polarization inside the domains may remain unchanged. One must then be very careful in comparing experiments with theoretical predictions. No previous experiment gives any evidence for reduction in intrinsic polarization.

For the experimental verification of the intrinsic reduction of polarization values we have chosen a system in which depolarization effects cannot be sufficiently reduced by domain formation. We used ferroelectric triglycine-sulfate (TGS) films deposited on doped Si substrates[9] with Au as second electrode in a sandwich configuration. This particular system serves three purposes. (1) Since the important quantity is the ratio of the ferroelectric film thickness to the distance over which the compensation charges in the electrodes extend, we expect drastic changes of the intrinsic ferroelectric polarization even at film thicknesses on the order of 1 μm because of the

long screening length in semiconductors. (2) Since the space-charge extension can be readily changed in semiconductors, the effect of depolarization fields will be directly observable. (3) Because of the asymmetry of charge distribution for opposite polarization directions, depolarization effects cannot be avoided by domain formation as is explained below.

To rule out the influence of structural defects and impurities we compare loops taken under different depolarization conditions but in the same ferroelectric thin film, and do not compare loops taken in films of different thickness as was done previously.[7] For this purpose we needed a modification of the usual Sawyer-Tower circuit,[10] shown in Fig. 1. An electrometer amplifier with an input impedance of 10^{14} Ω between the oscilloscope and the capacitor C provides the dc coupling which is necessary to observe how opposite polarization directions are affected by the change of the depolarization conditions. These changes are brought about by illumination of the semiconductor electrode which changes the carrier concentration.

Figure 2 shows polarization-versus-voltage loops at 100 Hz in a 1-μm TGS thin film deposited on a p-type Si substrate with 10^{15} acceptors/cm^3. The polarity of the voltage is given with respect to the Au electrode. The fully saturated loop is shown for comparison, the "half-loop" is observed in the presence of depolarization fields. By comparing the two loops, we see that positive polarization values are totally suppressed and negative values are virtually unaffected. In contrast to the theory[5] which treated a symmetrical model and therefore predicted polarization reduction in both directions, in the experiment a distinction has to be made between the two polarization directions because of the asymmetry of the present system. Negative polarization values in Fig. 2 mean that the polarization vector points away from the p-type Si electrode which leads to hole accumulation. The accumulated holes are trapped by interface states which are present with a density on the order of 10^{14}/cm^2 eV as determined by photovoltage measurements.[11] In accumulation the charge distribution in the semiconductor is similar to that in the Au electrode. Depolarization effects at this film thickness are negligible and consequently the negative polarization is not reduced.

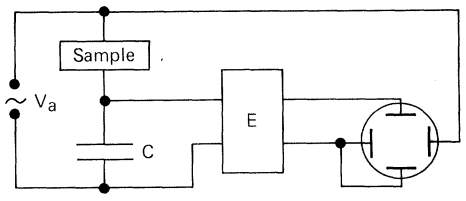

FIG. 1. Sawyer-Tower circuit modified by introducing electrometer E.

The compensation of positive polarization in Fig. 2 requires depletion of majority carriers in the semiconductor and accumulation of minority carriers. Since the minority carriers have to be generated thermally, which is a very slow process,[12] we can neglect their contribution to the total compensating charge at a frequency of 100 Hz. The region over which the compensating charge extends for the case of majority carrier depletion is larger than in the model used by Batra, Wurfel, and Silverman.[5] Depolarization effects should, therefore, be more pronounced in our experiment. This explains that in a 1-μm-thick ferroelectric film the positive polarization is totally unstable at room temperature as seen in Fig. 2.

The instability of the polarization in one direction could only be observed by comparison with saturated loops taken with the same sample. To obtain the saturated loop in Fig. 2 we reduced the space-charge width by generating minority carriers at a faster rate by high-intensity illumination of the semiconducting electrode. These minority carriers are then trapped by surface states so that under illumination, depolarization effects are negligible for both polarization directions. The sample was illuminated through a light chopper which was synchronized with the applied voltage in such a way that always two loops were tak-

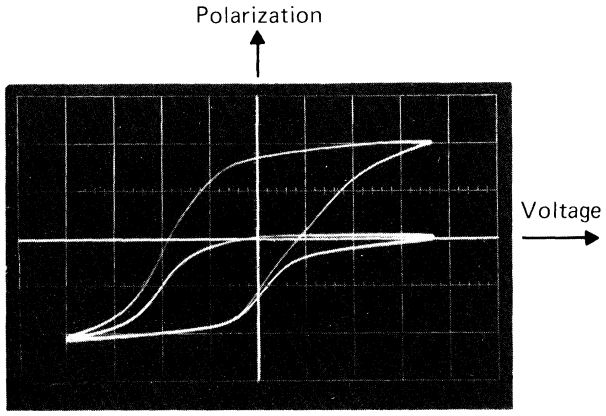

FIG. 2. Polarization loops in a thin TGS film sandwiched between a gold and a p-type (10^{15} acceptors/cm^3) silicon electrode.

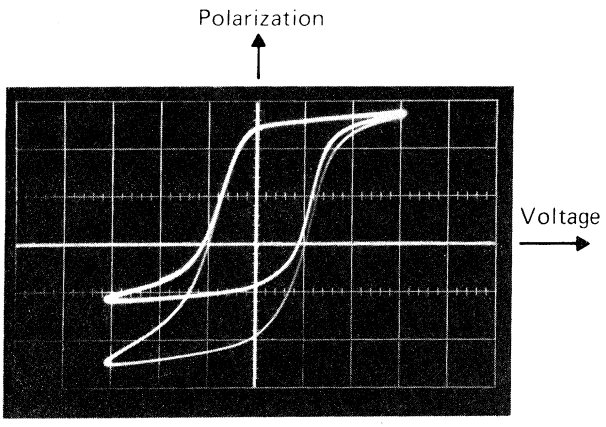

FIG. 3. Polarization loops in a thin TGS film sandwiched between a gold and an n-type (10^{17} donors/cm^3) silicon electrode.

en in the dark showing the effect of depolarization fields and for every third loop the sample was illuminated eliminating the depolarization fields. Upon illuminating the electrode the loop expands only in one direction, showing that the polarization was unstable in this direction in the dark. Since even in the dark the RC time for supplying the compensation charges is less than 10^{-5} sec, it is ensured that all of the applied voltage drops across the ferroelectric during the loop measurement.

The above considerations are supported by loops taken in a TGS film with an n-type semiconducting electrode with 10^{17} donors/cm^3 shown in Fig. 3. By comparison with the saturated loop we see that now the negative polarization values, which require depletion of majority carriers (electrons), are reduced by depolarization, but the instability is not as severe as in Fig. 2 because the higher doping density provides better compensation of the polarization. Positive values of polarization which are compensated by majority carrier accumulation are not affected.

As pointed out earlier, the observation of reduced polarization values does not always mean that the polarization is reduced intrinsically. In symmetric configurations with two identical electrodes, depolarization fields can be avoided by the formation of domains, because the depolarization fields from adjacent domains of opposite polarization cancel each other. The *average* polarization is reduced, but the intrinsic polarization inside the domains is unaffected. As a result of the asymmetry in our system, however (one polarization direction completely compensated by majority carrier accumulation, the other poorly compensated by carrier depletion), only one polarization direction is accompanied by depolarization fields. Thus in our system the formation of domains does not lead to a cancelation of the depolarization fields from adjacent domains, but on the contrary it increases the total energy of the system by the energy of the domain walls. The formation of domains is therefore energetically unfavorable, and consequently in our system the lowest energy state is achieved by reducing the polarization intrinsically.

These experiments prove the existence of depolarization fields in thin ferroelectric films, and for the first time we have succeeded in demonstrating experimentally that the polarization is drastically reduced in thin ferroelectric films. Furthermore we have eliminated the influence of impurities, structural defects, and domain formation.

The authors wish to thank Dr. R. Ferrier and Dr. D. Treves for a critical reading of the manuscript. One of us (P.W.) would like to express his sincere appreciation to IBM for the opportunity to work at the San Jose Research Laboratory.

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[1]P. G. de Gennes, Rev. Mod. Phys. 36, 225 (1964); W. L. McMillan, Phys. Rev. 167, 331 (1967); M. Strongin, O. F. Kammerer, J. E. Crow, R. D. Parks, D. H. Douglass, Jr., and M. A. Jensen, Phys. Rev. Lett. 21, 1320 (1968); J. M. Dickey and A. Paskin, Phys. Rev. Lett. 21, 1441 (1968); M. Strongin and O. F. Kammerer, J. Appl. Phys. 39, 2509 (1968); M. Strongin, R. S. Thompson, O. F. Kammerer, and J. E. Crow, Phys. Rev. B 1, 1078 (1970); P. B. Allen and M. L. Cohen, Phys. Rev. Lett. 29, 1593 (1972); M. Strongin, O. F. Kammerer, H. H. Farrell, and D. L. Miller, Phys. Rev. Lett. 30, 129 (1973).

[2]E. Guyon and C. D. Mitescu, Thin Solid Films 12, 355 (1972).

[3]V. L. Ginzburg and L. P. Pitaevskii, Zh. Eksp. Teor. Fiz. 34, 1240 (1958) [Sov. Phys. JETP 7, 858 (1958)]; E. Long and L. Meyer, Phys. Rev. 85, 1030 (1952).

[4]C. A. Neugebauer, Phys. Rev. 116, 1441 (1959); R. Baron and R. W. Hoffman, J. Appl. Phys. 41, 1623 (1970); J. C. Walker, in Proceedings of the Eighteenth Annual Conference on Magnetism and Magnetic Material, Denver, Colorado, 28 November–1 December 1972 (to be published).

[5]I. P. Batra, P. Wurfel, and B. D. Silverman, Phys. Rev. Lett. 30, 384 (1973).

[6]I. P. Batra and B. D. Silverman, Solid State Commun. 11, 291 (1972); B. M. Vul, G. M. Guro, and I. I. Ivanchik, Fiz. Tekh. Poluprov. 4, 162 (1970) [Sov. Phys. Semicond. 4, 128 (1970)]; R. R. Mehta, B. D. Silver-

man, and J. T. Jacobs, Bull. Amer. Phys. Soc. 17, 103 (1972); P. Wurfel and I. P. Batra, *ibid.* 17, 1182 (1972).
[7]H. Shibata and H. Toyoda, J. Phys. Soc. Jap. 17, 404 (1962).
[8]V. P. Dudkevich *et al.*, Izv. Akad. Nauk USSR, Ser. Fiz. 35, 1952 (1971) [Bull. Acad. Sci. USSR, Phys. Ser. 35, 1773 (1971)]; V. G. Gavrilyachenko, V. P. Dudkevich, and E. G. Fesenko, Kristallografiya 13, 342 (1968) [Sov. Phys. Crystallog. 13, 277 (1968)].
[9]J. T. Jacobs and K. Keester, to be published.
[10]C. B. Sawyer and C. H. Tower, Phys. Rev. 35, 269 (1930).
[11]P. Wurfel and W. Ruppel, in *Proceedings of the Third International Conference on Photoconductivity, Stanford, California, 1969* (Pergamon, New York, 1972), p. 379.
[12]S. R. Hofstein and G. Warfield, Solid State Electron. 8, 321 (1965).

Nuclear Reactions of V with 300-GeV Protons and Co with 11.5-, 200-, and 300-GeV Protons*

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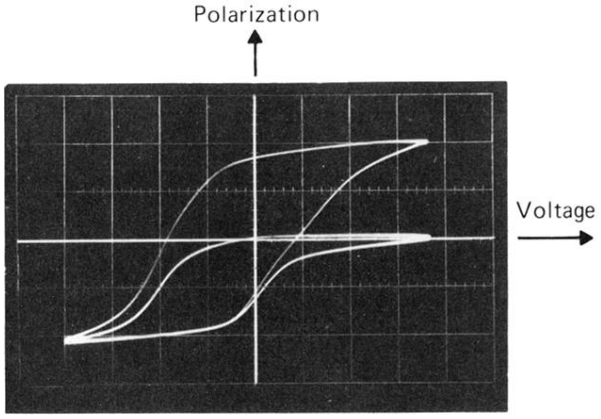
Cross sections of a large variety of spallation products from V and Co do not change appreciably as the beam energy increases from 11.5 to 300 GeV. The mean ratio σ_{300}/σ_{29} for V is 0.96 ± 0.04; for Co, $\sigma_{200}/\sigma_{11.5} = 0.95 \pm 0.06$ and $\sigma_{300}/\sigma_{11.5} = 1.02 \pm 0.09$. It was assumed that the monitor cross section is constant above 10 GeV.

We are reporting the first measurements of spallation cross sections for 200- and 300-GeV protons. Similar studies have been carried out previously on a number of target nuclei at energies up to 29 GeV, and have been summarized in a recent review article.[1] The 200- and 300-GeV irradiations were performed in an external proton beam in the neutrino hall at the National Accelerator Laboratory (NAL). The vanadium targets were analyzed at Brookhaven National Laboratory (BNL) and the cobalt targets at Argonne National Laboratory (ANL). Two irradiations of Co were also done with 11.5-GeV protons in the circulating beam of the ANL zero-gradient synchrotron so that a direct comparison could be made of the higher-energy results with data from the energy region investigated previously. A detailed study of the nuclear reactions of V at 3 and 29 GeV was recently completed.[2]

The target foils (6×6 cm^2) were irradiated together with aluminum monitor foils, and each was sandwiched between guard foils to avoid cross contamination and to compensate for recoil effects. The total thickness of each Co foil stack was ~100 mg/cm^2; two of the V stacks were ~150 mg/cm^2, and the third was ~30 mg/cm^2. The beam intensity varied from 10^{10}–10^{11} protons/pulse and irradiation times were 8–21 h. An area of 2–3 cm^2 of each stack was punched out for counting; nearly all of the radioactivity was within this area. The aluminum monitor foils were counted to determine the amount of ^{24}Na formed. The V and Co target foils were counted without any chemical separation with calibrated Ge(Li) spectrometers of 4096 channel capacity and magnetic-tape readout. The more intense characteristic γ rays of each radioactive product were measured at various times after bombardment in order to establish that they decayed with the correct half-life; V samples were followed for 1 month, and Co samples for at least 2 months after irradiation. The spectra were analyzed by means of a computer program[3] which found all significant peaks and computed their areas and decay rates. The nuclides were identified unambiguously by their γ-ray energies and half-lives. Disintegration rates were computed from measured photopeak intensities, the calibrated photopeak efficiencies of the detector, and known γ-ray abundances.[4,5] When necessary, corrections were made for summing of coincident γ rays. In order to calculate product cross sections from disintegration rates, it was assumed that ^{24}Na is produced in the Al monitor with the same cross section as at 10–28 GeV, i.e., 8.6 mb.[6]



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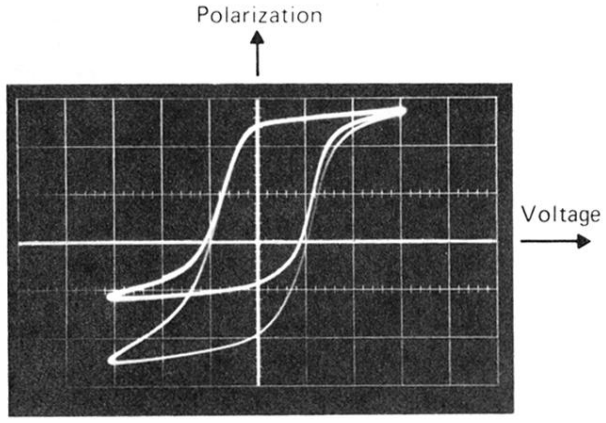

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