Charge Pumping and Pseudopyroelectric Effect in Active Ferroelectric Relaxor-Type Films

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Unidirectional charge flow was observed in potassium tantalum niobate, $KTa_{0.6}Nb_{0.4}O_3$, films. These films of relaxor-type diffuse phase transition material were formed by metalorganic deposition and had a polarization gradient normal to the surface of the films. Novel charge pumping was observed in the active operation of simple two-terminal structures by excitation with periodic, strong electric fields. Such operation also showed a large pseudopyroelectric response. Effective pyroelectric coefficients as large as 2×10^{-5} C/cm^2°C have been obtained.

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Ferroelectric materials are inherently nonlinear and ideally can demonstrate virtually square hysteresis [1]. In some cases a clear threshold in polarization reversal is observed [2]. The electric displacement D, or the charge state of the matter, is primarily a function of electric field (E), temperature (T), and mechanical stress (σ), that is, $D=D(E,T,\sigma)$. Each independent variable may also be a function of time, permitting differentiation between bound charge (associated with spontaneous polarization) and free charge (due to the finite resistivity of the dielectric).

Historically, ferroelectric materials have generally been characterized by weak-field (or small-signal) analyses, which have led to the common descriptors of permittivity, pyroelectric coefficient, and piezoelectric constant [3]. Some of the most useful applications of ferroelectric devices, however, require nonlinear operation at or near coercive field strengths, where these descriptors are invalid.

In this Letter we show how the application of strong alternating fields to a graded polarization relaxor-type ferroelectric film leads to the new phenomenon of unidirectional charge flow. These graded structures show continuous charge pumping at a rate which is not only monotonically dependent upon the applied field but has a very strong temperature dependence. This behavior was observed in the active operation of simple two-terminal structures by excitation with periodic, strong electric fields.

Films of potassium tantalum niobate, $KTa_{0.6}Nb_{0.4}O_3$ (KTN), were formed on platinum-coated polycrystalline yttria [4] by metalorganic deposition [5,6]. Metal carboxylates of Ta and Nb were synthesized by reaction of the metal ethoxides with neodecanoic acid. Potassium neodecanoate was synthesized by reacting KOH with neodecanoic acid. As formed, the neodecanoate compounds were all highly viscous materials which dissolved readily in xylene. Individual solutions of the metal neodecanoates were combined in the desired proportions to form multimetal carboxylate solutions. Film composition was altered by adjusting the proportions of the single neodecanoate solutions which went into the carboxylate mixture. Rutherford backscattering spectrometry, electron-microprobe analysis, and x-ray analysis were used to determine the film composition and crystalline phases.

After flooding the platinum surface of yttria substrates with the combined solutions, the substrates were spun at 2000 rpm for 30 s. This process uniformly dispersed the liquid over the surface of the platinum and volatilized the xylene, leaving a tacky organic layer a few micrometers thick. The substrate and corresponding organic film were positioned on either a quartz or silicon setter and then placed into a muffle furnace. Pyrolysis was carried out at 600 °C for 300 s in air. Spin-coating and pyrolysis were repeated as many as 40 times to build up the thickness of the films. After final pyrolysis, the yttria substrates on zirconia setters were placed in platinum crucibles for annealing. Surrounding the setters was a potassium aluminate powder which was a source of potassium vapor at the annealing temperature of 1100 °C [7]. After annealing at 1100 °C for 24 min the samples were reannealed in oxygen at 900 °C for 60 min. From scanning electron microscopy the films were found to be quite uniform, with 1-2-μm-size grains, and little apparent porosity.

Circular Au/Cr electrodes were deposited on the surface of the KTN films by e-beam evaporation. The nominal contact area was 0.012 cm^2 and consisted of a 40-nm Cr underlayer followed by a 300-nm overlayer of Au. Electrical contact was made to the platinum layer to serve as the counter electrode.

Measurements of the permittivity as a function of temperature were made using an impedance analyzer and a vacuum chamber with a regulated temperature control system [8]. A 5-kHz sine wave at 1 mV$_{\mathrm{rms}}$/μm was used as the test signal. Hysteresis measurements were made using a modified Sawyer-Tower circuit [9] with differential inputs feeding into a dc-coupled x-y oscilloscope.

The relative permittivity κ is defined by the relation $\kappa\equiv(1/\epsilon_0)(\partial D/\partial E)_{E=0}$, where ϵ_0 is the permittivity of free space. In Fig. 1, the measured κ for a typical 9.8-μm KTN film is plotted as a function of temperature with E-field bias as a parameter. A broad peak centered at 5 °C is observed with a peak relative permittivity of 5000; the shifts in the position of the dielectric peak with applied bias are consistent with a normal ferroelectric. In comparison to the thin-film measurements, plots of κ as a

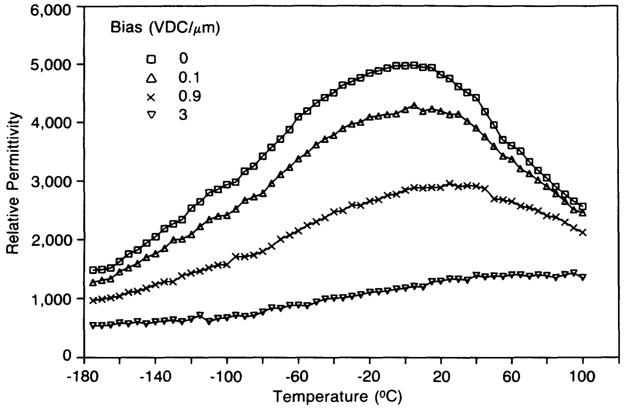

FIG. 1. Permittivity as a function of temperature and electric-field bias for a 9.8-μm-thick KTN film.

function of temperature and field for single-crystal KTN revealed a large peak relative permittivity (21 000) with a sharp transition from the cubic to tetragonal phase at 0 °C [10]. Plots of the conventional pyroelectric coefficient as a function of temperature for the KTN films show some variation but have a typical value (below 10 °C) of 1×10^{-8} C/cm^2°C.

In Fig. 2 an unconventional hysteresis phenomenon is shown. The set of open loops was obtained for a KTN film held at 37.5 °C and generated using a 50-Hz triangular wave. This set of loops, which do not close upon themselves, was obtained from 35-V_p (peak) excitation. This charge pumping action is observed as a dc component in the electric charge versus time wave form across the serially connected integrating capacitor of the modified Sawyer-Tower circuit.

In Fig. 2 the hysteresis loops have developed large offset components in electric displacement, ΔD, and represent a total charge storage of 2.4×10^{-5} C/cm^2 for $V_p=35$ V after ten voltage cycles, or 0.2 s. The charge offset was found to increase proportionally with V_p. For this device, ΔD saturated at a maximum value equal to 2.64×10^{-4} C/cm^2 after several seconds for 35 V_p. Hysteresis was found to persist well above the nominal Curie temperature (measured as high as 100 °C), consistent with reported observations on other diffuse phase transition perovskite structures [11-13].

The sense of the offset was always the same and was found to be intrinsic to the film orientation and structure. Removal of the yttria substrate and platinum overcoat by selective etching was used to create a self-supporting KTN film. When the Au/Cr contacts were deposited on the surface of the KTN previously joined to the platinum layer, the direction of the response relative to these contacts was found to reverse. That is, there was a directionality relative to the film even with metallically symmetric contacts. Substitution of the Au/Cr and platinum electrodes by other metals such as In, Cr, Cu, or Al did not significantly alter the results. By means of a large number of experiments we were also able to rule out rectification at either contact as the cause of the charge offsets.

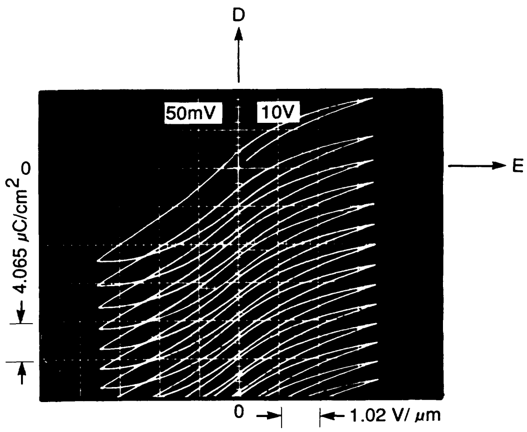

FIG. 2. Unconventional hysteresis phenomenon in D vs E plots, obtained at 37.5 °C by excitation with a 35-V_p, 50-Hz triangular wave. This behavior was observed in a 9.8-μm-thick KTN film.

Figure 3 shows how the charge offset varies with temperature. The applied ac voltage is a 34-V_p, 1-kHz sine wave. Here, the vertical scale of the oscilloscope has been reduced to adequately record the large translation of the hysteresis loop with temperature. Because of the reduced gain of the oscilloscope, the hysteresis loops appear only as lines on the scope traces. The translation of the loop varies rapidly with temperature. An effective, or pseudo, pyroelectric coefficient for this device can be defined as $p_{\text{eff}}\equiv(1/A)\Delta(\Delta Q)/\Delta T$, where $\Delta(\Delta Q)/\Delta T$ is the change in offset charge stored on the ferroelectric capacitor (loop translation) for a change in temperature, ΔT.

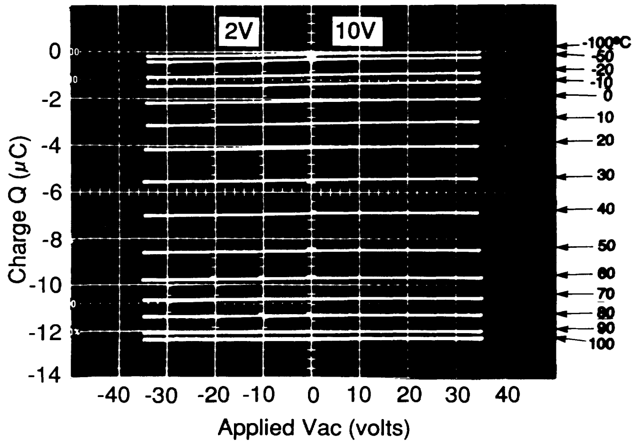

FIG. 3. Variation in charge offset as a function of temperature. The applied ac voltage is a 35-V_p, 1-kHz sine wave. The vertical gain of the oscilloscope has been reduced so low that the hysteresis loops appear only as lines.

Figure 4 shows the temperature dependence of $p_{\rm eff}$. Note that $p_{\rm eff}$ peaks at 1.2×10^{-5} C/cm^2°C, much greater in magnitude than the conventional pyroelectric coefficient found in the best KTN single crystals. The $p_{\rm eff}$ is seen to have a strong temperature dependence with a maximum at the point of maximum $d\epsilon/dT$, above the nominal Curie temperature. Pseudopyroelectric coefficients as high as 2×10^{-5} C/cm^2°C have been observed for some of our films. A weak frequency dependence is observed in $p_{\rm eff}$, with a variation on the order of 6 dB over the frequency range 1–100 kHz, but with a clear maximum usually in the low kHz region.

Under alternating field excitation the integrating capacitor acquires a static energy, that is, ΔD reaches a maximum value. However, if a resistive load shunts the integrating capacitor, the ferroelectric device acts to maintain this static charge. Thus, the device acts as a "charge pump," delivering continuous power into the resistive load provided the temperature of the ferroelectric is held constant. The amount of charge flow at steady state is a direct measure of the temperature of the ferroelectric device. An incremental change in heat energy to or from the device is detectable by a change in output power level as supplied by the field excitation, thus making this an active device.

Over the temperature range investigated, -100 to 100°C, the actions of charge pumping and thermal response were dependent upon the chemical composition of the films. Thin films [14] of $KTaO_3$ ($T_c\sim13$ K) [15] showed neither charge pumping nor thermal response, while films [14] of $KNbO_3$ ($T_c=435$°C) [15] showed only charge pumping and no thermal response.

Translations of hysteresis loops along the field axis are well known [16,17] and have been attributed to crystal defects and imperfections. In addition, antiferroelectric behavior [18], lossy ferroelectrics [19], rectifying contacts [20], and mechanical constraint of a ferroelectric [21] can all produce distortion in hysteresis loops. Although shifts in the offset charge have previously been observed [21,22], to our knowledge, variable alternating field-induced charge offsets and their strong temperature dependence represent entirely new phenomena.

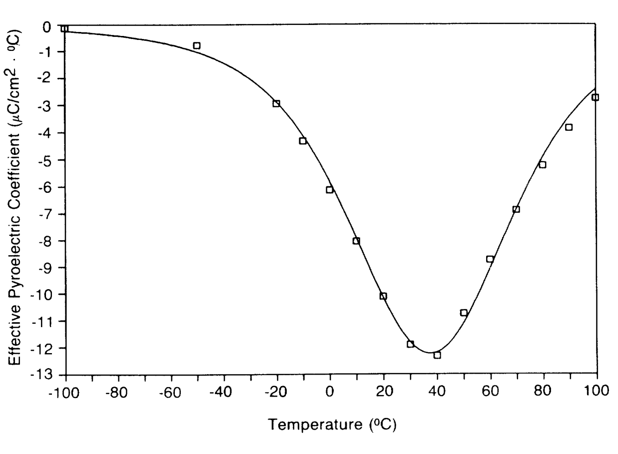

FIG. 4. Effective, or pseudo, pyroelectric coefficient, $p_{\rm eff}=(1/A)\Delta(\Delta Q)/\Delta T$, at 1.0 kHz and 35 V_p for a 9.8-μm-thick KTN film.

The existence of a hysteresis loop in a material held above its Curie temperature, other than in diffuse phase materials, has previously been observed [22,23]. It has been suggested that the loops arise from a surface layer less than 1 μm thick. This surface layer was found to remain in the tetragonal structure at temperatures well above that where the body of the material had already relaxed back into the cubic structure. Such a layer would be polarizable and could account [24] for the distortions seen in the low-frequency I-V characteristics of our KTN films. Our initial attempts to discover the origin of the charge pumping and thermal response of the KTN capacitor devices thus focused on KTN surface properties.

Attempts to scrape, grind, or acid etch away any anomalous KTN surface layer, however, proved inconclusive. Shaving the surface of an 8-μm-thick KTN film by razor blade scraping or mechanical grinding did not noticeably affect the charge offset per unit area per applied alternating field, $\beta\equiv(\Delta Q/A)/(V_p/t)\equiv\Delta D/E_p$, where t is the thickness of the film. Etching a 12-μm-thick KTN film for 10 min in a 50:50 solution of H_2O and concentrated HF, however, did reduce $\beta(T=100$ °C) from 1.2×10^{-9} to 7.15×10^{-12} C/V cm. In all cases hysteresis loops were observed at 100°C [25]. Differential surface profilometer measurements indicate that less than 700 nm were removed by the 10-min etch. A 20-min etch produced films which were electrically shorted to the platinum surface. These etching experiments indicate that HF primarily attacks the grain boundaries of the KTN films.

Other experiments strongly pointed to a surface origin for the charge pumping and thermal response. For two KTN films, 9.8 and 16 μm thick, respectively, β was greater in the thinner film. At 100°C, $\beta_{9.8\,\mu\rm m}=7.28\times10^{-9}$ C/V cm and $\beta_{16\,\mu\rm m}=8.9\times10^{-10}$ C/V cm for the two films.

Finally, it was found that 74-μm-thick single crystals of KTN [10] (which had a Curie temperature of 0°C) also showed both charge pumping and thermal response. At 0°C, the crystals had $\beta=7.2\times10^{-10}$ C/V cm and a directionality. That is, the sense of the effect, relative to the KTN crystal, did not reverse when the crystals were stripped of their electrodes and the positions of the Au/Cr contacts (0.012 cm^2) and ground plane were interchanged.

Electron-microprobe analysis of both sides of the KTN crystals revealed no difference in the Ta-to-Nb ratio. There was, however, a 0.7 at.% variation in potassium concentration (relative to Ta and Nb) through the 74-μm-thick crystals. This result is not surprising as the crystals were grown in the presence of excess K_2O. During crystal growth, loss of K_2O was evident. Chemical analysis of the KTN films also revealed a potassium concentration gradient. X-ray photoemission spectroscopy depth profiling showed that the potassium concentration in the films varied by 5.6 at.% over a 2-μm depth with the greatest potassium concentration at the film surface. The Ta/Nb ratio in the films was constant throughout the 2 μm. Again, this result is quite reasonable as the films were annealed at 1100 °C in the presence of excess potassium vapor.

It appears that a plausible explanation for the charge pumping and its temperature sensitivity must be related to the gradient in potassium concentration. This conclusion is further strengthened by the fact that charge pumping and pseudopyroelectric effects were also observed in films [14] bearing lead (Pb) but not in films [14] or bulk ceramics of uniform composition with nonvolatile elements, such as barium titanate or barium strontium titanate (BST). We did, however, observe temperature-dependent charge pumping in films of BST with a graded composition, hence graded polarization. We found the sense of the pumping to be dependent upon the direction of the grade.

We believe that a potassium concentration gradient leads to a gradient in the solid solutions of $KNbO_3$ to $KTaO_3$ with greater $KNbO_3$ in the potassium-rich regions of the film. Potassium-deficient regions are believed to be a mixture of $KTa_{1-x}Nb_xO_3$ (x variable) and Ta_2O_5 rich phases which were detectable by x-ray analysis. It is the relative ratio of $KNbO_3$ to $KTaO_3$ which determines the Curie temperature of KTN [26]. Clearly, a gradient in this ratio will lead to a distribution in Curie temperatures and hence to a distribution in the spontaneous polarization. To conclude that there exists a gradient in Curie temperatures is not unreasonable given the broadness of the curve in Fig. 1. Thus, the KTN films would be relaxor-type material [11-13] by virtue of their layered structure. A mere distribution in spontaneous polarization may, however, be insufficient to account for the anomalous effects we have observed. We have not determined the combined effects of a polarized surface layer [24] and a gradient in spontaneous polarization with an attendant gradient in dipole moment, nor the effect of polarization pinning in the individual layers by polar defects [13].

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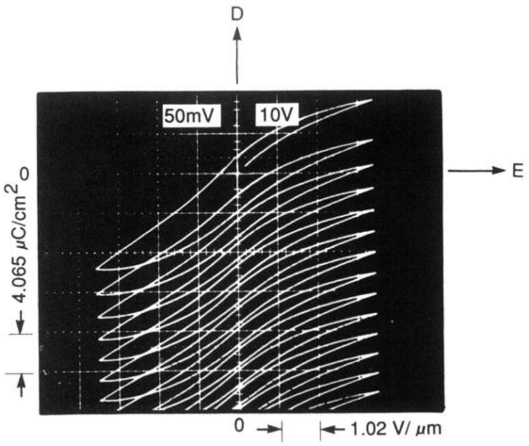

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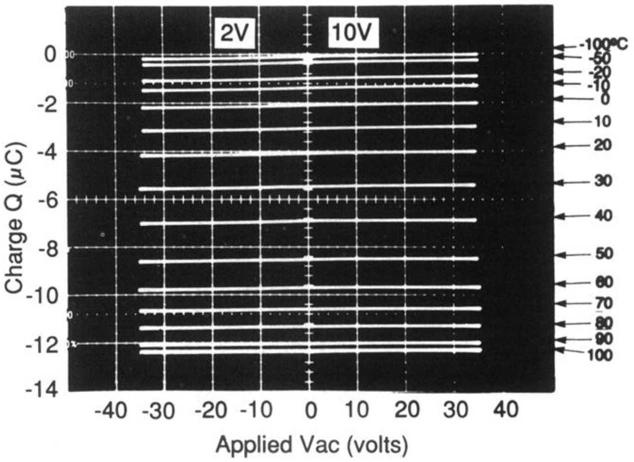

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