Pyroelectric Effect Induced by the Built-In Field of the $p-n$ Junction in the Quantum Paraelectric PbTe: Experimental Study

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We report here the first observation of a pyroelectric effect in a nonpolar semiconductor. This effect originates in the temperature-dependent electric dipole of the PbTe $p-n$ junction. The junction was illuminated by a chopped CO_2 laser beam, and periodic and single-pulse pyroelectric signals were observed and measured as a function of temperature, reverse bias voltage, and chopper frequency. The measured pyroelectric coefficient is $\approx 10^{-3}\ \mu C/cm^2\,K$ in the region of 40–80 K. The theoretical model describes quantitatively all experimental features. The time evolution of the temperature inside the junction region was reconstructed.

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The standard pyroelectric effect (PE) is observed only in crystals having polar axis symmetry [1]. However, in any nonpolar solid, a built-in electric field, such as in the semiconductor barrier structures, $p-n$ junctions (PNJ), Schottky contacts, heterojunctions, etc. [2], creates a polar direction and an electric dipole moment. If the dipole moment of the depleted area of PNJ varies with temperature, it can generate a pyroelectric effect, the junction barrier pyroelectricity (JBP). The magnitude of the JBP effect will be large, provided that the static dielectric constant ϵ of the semiconductor depends strongly on temperature. Quantum paraelectrics, such as $SrTiO_3$ [3] or the narrow band semiconductor PbTe [4,5], possess this property [6].

For the observation of JBP, high-quality diodes have been prepared on a rectangular slice, cut from a p-PbTe single crystal, grown by the Czochralski method. The acceptor concentration was 10^{18} cm^{-3}. At 80 K the hole diffusion length was $\approx 30\ \mu$m, and the mobility was ≈ 14500 cm^2/V $\cdot$ s at 80 K. The PbTe absorption coefficient at the wavelength of 10.5 μm, with a carrier concentration of 10^{17}–10^{18} cm^{-3}, is $\alpha \approx 10^2$ cm^{-1} in the temperature interval of 20–200 K [7].

The n region was created by thermodiffusion of indium from In_4Te_3 gas phase. PNJ was formed at a depth of $\approx 70\ \mu$m below the surface. The details of the sample preparation methodology, and the detailed account of the characterization of these diodes, will be published elsewhere [8,9].

The current-voltage characteristics fitted by the Shockley formula [2] provided an ideality factor ≈ 1.5–2 and a saturation current density 10^{-5} A/cm^2 at 80 K. The junctions were found to be linearly graded [2]. The temperature dependence of the dielectric constant $\epsilon(T)$, derived from the temperature dependence of the junction capacitance, is fitted by Barrett's formula [10]:

$$\varepsilon = \frac{1.36 \times 10^5}{36.14 \times \coth(36.14/T) + 49.15}. \tag{1}$$

The junction was illuminated by a chopped CO_2 laser beam, and the observed pyroelectric response was measured as a function of temperature, reverse bias voltage, and chopper frequency. The experimental setup for measuring the pyroelectric signal (PES) is shown schematically in Fig. 1. The PES temporal variation has been measured by a Tektronix Differential Preamplifier ADA400A and displayed on a Tektronix e-Scope TDS 3054B. The PES under bias, V_b, has been measured by an EG&G Princeton Applied Research Lock-In Amplifier 5209, in

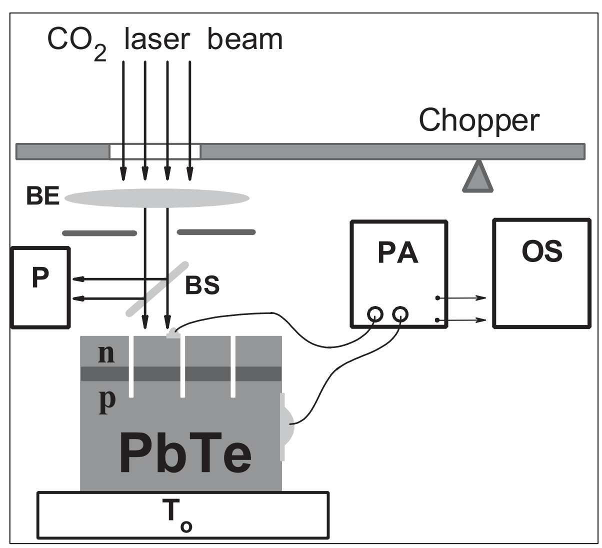

FIG. 1. Schematic drawing of the experimental setup. BE—beam expander; BS—beam splitter; P—light intensity monitor; PA—preamplifier; OS—oscilloscope; T_0—temperature set by the temperature controller.

parallel with a Keithley Sourcemeter 2410 for applying V_b. The output signal was displayed on the e-Scope. The signal was found to depend linearly on the laser beam intensity P. Maximal laser intensity was $\sim 1\ \mathrm{W/cm^2}$. The chopper frequency f was varied from 4 to 2000 Hz. The width of the chopper slit was much larger than the lateral width of the junction. Therefore, the time dependence of the light intensity on the illuminated area was trapezoidally shaped, with short rise and fall times and a long period of constant illumination or darkness.

The excitation was applied in two modes: (1) a periodic mode (PPES) with equal durations of illumination and darkness; the period was shorter than the characteristic times of the temperature relaxation (t^*) and $t_e = RC$ of the diode; (2) a single-pulse mode with a long darkness period, so that the temperature and RC relaxations have been completed before the occurrence of the next pulse.

The measurements were performed over the temperature interval 12–130 K. The samples were placed in a He-gas closed cycle refrigerator cryostat, in a vacuum of about 10^{-7} Torr. The temperature was controlled and stabilized by a LakeShore DRC-91CA temperature controller.

The JBP theory is constructed, akin to the standard theory of PE for thin pyroelectric films [11–13], with specific attention to the junction depleted region [2]. The PE theory is based on the simultaneous solution of a pair of coupled equations: the thermal balance equation and the Kirchoff's equation for the quasistationary currents. The thermal balance is given by the equation

$$C_T \frac{dT}{dt} + G_T \Delta T = A(t)P, \qquad (2)$$

where C_T is the total heat capacity of the junction, G_T is the heat transfer coefficient, $A(T)$ is the illuminated sample area, and P is the laser power, $\Delta T = T - T_0$, where T is the junction temperature and T_0 is the temperature as set by the temperature controller (Fig. 1). The term $G_T \Delta T$ describes the Newton heat transfer.

The equation for the current is

$$\frac{d[C(V_t)V_t]}{dt} + \frac{U}{R(V_t)} = 0, \qquad (3)$$

where $V_t = V_0 - V_b + U$, V_0 is the built-in barrier potential, and U is the PES. Typical value of V_0 is a few tens of mV, and of V_b a few hundreds of mV. Since U (of the order of μV) is much less than both V_0 and $|V_b|$, one can expand the terms in Eq. (3) into a power series in U, keeping linear terms only. Then, designating $V = V_0 - V_b$, we obtain

$$\frac{dU}{dt} + \frac{U}{R(V)C(V)} = \Lambda \frac{dT}{dt}; \qquad \Lambda = -V \frac{d \ln C(V)}{dT}; \qquad \lambda = \frac{\Lambda}{A_e}, \qquad (4)$$

where A_e is the area of the junction. Thus, Λ is the PE coefficient of JBP, and λ is the ordinary PE coefficient [14].

Equation (4) shows that JBP is zero when the PNJ barrier vanishes ($V_0 = 0$). From Eq. (4) it also follows that the value of Λ depends on the level of doping (via V_0), on the doping gradient (via C), on $\varepsilon(T)$ (via C), on V_b, and on T_0. The graph of λ (at constant V_b) vs T is shown in Fig. 2. The value of the pyroelectric coefficient λ is $\approx 10^{-3}\ \mu\mathrm{C/cm^2\,K}$ in the region of 40–80 K, λ being negative in accord with $d\varepsilon/dT < 0$ [Eq. (1)].

The solution of the coupled Eqs. (2) and (4) is determined by three parameters: $t^* = C_T/G_T$, $p = t^*/RC$, and Λ.

The left-hand side of Eq. (4) consists of two currents

$$I_1 = C(V)\frac{dU}{dt} \quad \text{and} \quad I_2 = \frac{U}{R(V)}. \qquad (5)$$

I_1 is the displacement current due to the change of the PNJ dipole moment; I_2 is the conduction current, screening the nonequilibrium PNJ polarization charges.

Equation (4) can be applied also independently on Eq. (2), to deduce $\Delta T(t)$ in the PNJ for an arbitrary, JBP generating source. Indeed, if the PES $U(t)$ is measured, then Eq. (4) gives for dT/dt

$$\frac{dT}{dt} = \frac{C(V)}{\Lambda}\frac{dU}{dt} + \frac{U}{R(V)\Lambda}. \qquad (6)$$

Integrating Eq. (6) one can find $\Delta T(t)$.

Figure 3 shows an example of the measured and calculated time variation of PPES at $T = 80.1$ K, at different frequencies and at $V_b = 0$. The calculated shape of PPES agrees well with the experiment.

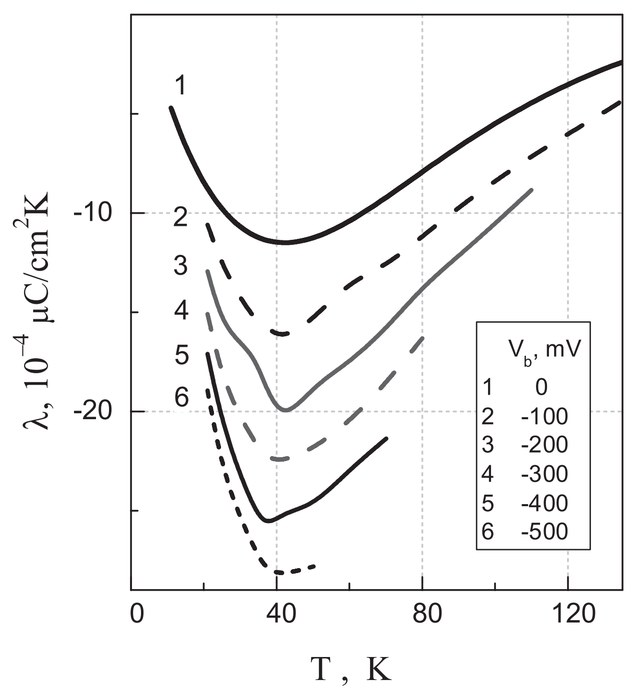

FIG. 2. The temperature dependence of the PE coefficient at different bias voltages.

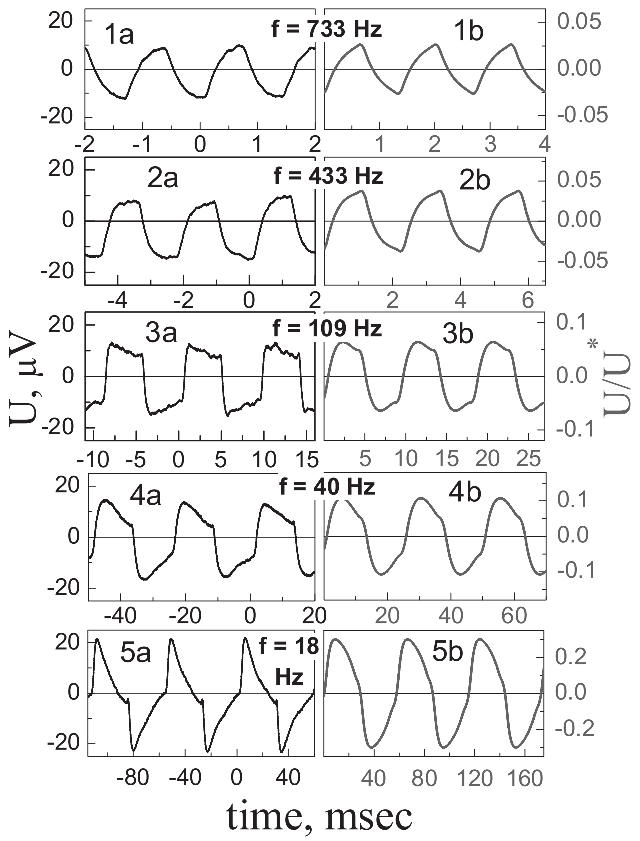

FIG. 3. The pyroelectric signal at 80.1 K and at different chopper frequencies. (a) experiment; (b) theoretical calculation (in normalized units).

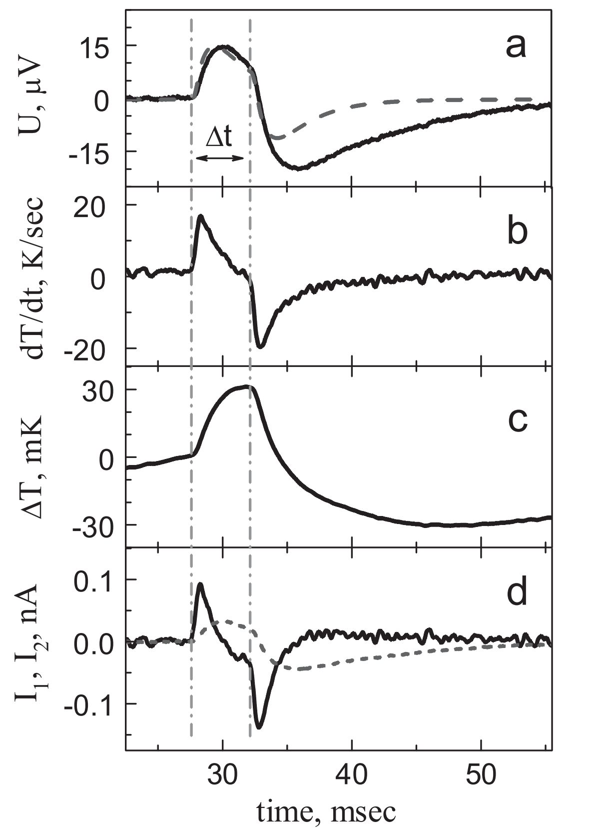

FIG. 4. The time evolution of the single-pulse excitation response, reconstructed with Eq. (6), at 60.2 K, of: (a) $U(t)$ (solid line, experimental; dashed line, calculated); (b) the rate of change of the temperature inside PNJ; (c) time evolution of the temperature in PNJ; (d) the displacement current I_1 (solid line) and the conduction current I_2 (dashed line). $\Delta t = 4.6$ msec, the time between pulses is 50 msec.

The main features of these time-dependent variations are: (1) the PPES exhibits the typical ''pyroelectric'' shape and the magnitude of PPES is $\sim$10–20 μV; (2) the PPES shape varies rather markedly with frequency; (3) PPES changes sign in the dark phase; (4) the PPES amplitude drops with increasing temperature, since the built-in barrier V_0 vanishes at higher temperatures and $\Lambda \rightarrow 0$; (5) the PPES amplitude increases with the reverse bias, as Λ increases with V_b (Fig. 2).

The single-pulse response behaves similarly.

Figure 4 shows the time evolution [reconstructed using Eq. (6)] of the single-pulse excitation response, at 60.2 K and light intensity 1330 mW/cm^2, of: (a) the single-pulse mode, $U(t)$; (b) the rate of change of the temperature, dT/dt; (c) the temperature increment $\Delta T(t)$ within the PNJ; (d) the displacement and the conduction current kinetics, the screening current lagging after the displacement current, expressing the fact that I_1 initiates I_2.

The results for PPES, at the temperatures and frequencies of the experiment, lead to the following general conclusions. (1) The amplitude $\Delta T(t) \approx 10$ mK at low temperatures and reaches ≈ 1 K at higher temperatures. This is due to a decrease of the thermodiffusivity at higher temperature. Respectively, the heat transfer between the PNJ and the adjoining medium decreases. (2) For the same reason, dT/dt increases also with temperature. (3) The current amplitude increases from 0.1 nA at low temperature to 1.5 nA at high temperature. At low temperature $I_2 \ll I_1$, and $I_2 \gg I_1$ at higher temperature, due to the exponential decrease of the PNJ resistance. (4) The delay of I_2 relative to I_1 is a result of general nature.

We observed a similar magnitude JBP also in a Schottky contact barrier of In-p-PbTe.

In conclusion, a pyroelectric effect in a PNJ of a nonpolar semiconductor was observed for the first time. The theoretical formulation describing the JBP has been successfully applied. The PES theory allows deducing the time variation of the temperature inside the PNJ. Other quantum paraelectrics, e.g., $SrTiO_3$, having a significantly larger dielectric constant and stronger temperature dependence than that of PbTe, are promising candidates for a large JBP and are presently investigated. JBP may be increased also using $p - n$ junction superlattices.

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[6] Any semiconductor barrier structure has always also a piezoelectric response (BPZE). Indeed, properties (doping concentration, dielectric constant, and energy spectrum) which determine the magnitude of the dipole moment depend on deformation. Also, internal friction during a real deformation inevitably induces a pyroelectric contribution. Those are inverse BPZEs, and, according to thermodynamics, direct BPZE must exist as well. Observation of BPZE, in an organic semiconductor Schottky contact, has been reported lately by G. Dennier *et al.*, Appl. Phys. Lett. **87**, 163501 (2005). It should be emphasized that BPZE is an inherent property of any barrier structure, not only in quantum paraelectric semiconductors. Also, a strong temperature dependence of the dielectric constant is not a condition for a large BPZE.
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[14] The dipole moment of the PNJ is a property of the junction region as whole, while that of the standard PE is determined by the dipole moment density. Therefore, Λ is the suitable characteristic parameter. The (small letter) λ is given only to enable a comparison with the standard PE.