Multiphonon recombination of carriers at frozen-photoconductivity centers in PbTe films

K. A. Baklanov and I. P. Krylov
Institute of Physical Problems, Academy of Sciences of the USSR

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A method involving a second illumination has established the existence of a metastable state of photoactive centers with a typical lifetime $> 10^6$ s. The temperature dependence of the recombination to the ground state indicates a pronounced local lattice deformation accompanying a change in the charge state of a defect.

Many phenomena which occur in semiconductors involve the formation of a metastable state of defects due to large local lattice deformations which accompany changes in the charge state of a defect.[1] One possible example is the frozen-photoconductivity effect, in which the decrease in the resistance which occurs during illumina-

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tion at low temperatures persists for an indefinitely long time after the light is turned off.[2] We have studied the increase in the conductance during the application of light (illumination) and the decrease in the conductance in darkness (relaxation) in PbTe films synthesized by vacuum deposition on glass substrates and cooled under standard atmospheric conditions. The thicknesses of the films lay in the range 400–1500 Å. We used a laser beam with a wavelength of 6300 Å and an intensity which corresponded to a photon flux density $I \approx 10^{15}$ cm$^{-2}\cdot$s^{-1} at the sample. At a fixed source voltage of 1.6 V we measured the current which passed through a film deposited between platinum contacts. The ratio of the width of the sample to its length was 10. The measurements were carried out over the temperature range $T = 4.2$–300 K.

A film cooled in darkness yielded a first-illumination curve similar to that shown in Fig. 1, which is described approximately at $T \leqslant 50$ K by the conductance expression $G \propto \log(1 + t/\tau_1)$. The time constant is $\tau_1 = 30$ s at $T = 4.2$ K. After the light is turned off, the relaxation can be described approximately by the expression $G/G_0 = 1 - A \log(1 + t'/\tau_1')$, where t' is the duration of the relaxation ($t' = t - 1200$ s in Fig. 1), and G_0 is the value of the conductance at $t' = 0$. Figure 2 shows the values of the coefficients A and τ_1' at various temperatures. In the experiments with longest

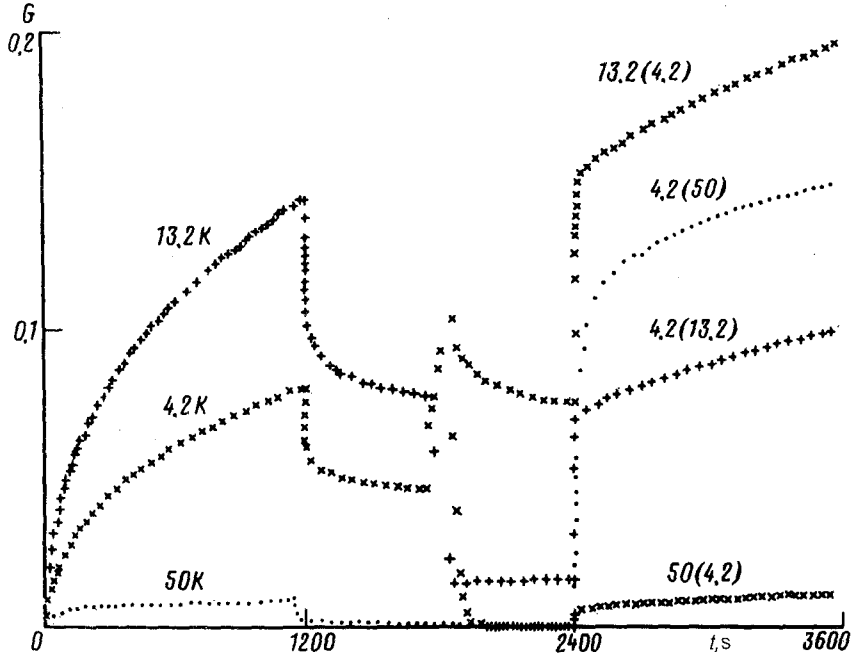

FIG. 1. The conductance, in units of $(\text{M}\Omega\cdot\text{cm})^{-1}$, during the first illumination ($0\text{ s} \leqslant t \leqslant 1200$ s) and during the second ($2400\text{ s} \leqslant t \leqslant 3600$ s) and during relaxation in darkness ($1200\text{ s} \leqslant t \leqslant 2400$ s) for film I, with a thickness $d = 400$ Å. The time, in seconds, is plotted along the t axis. The temperature T_1 is given for the region of the first illumination, T_2 is given for the second illumination, and T_1 is given in parentheses. The temperature was changed at the middle of the relaxation interval.

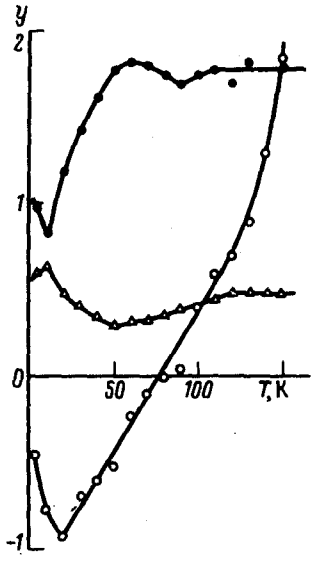

FIG. 2. Temperature dependence of the parameter is the relaxation formula $G/G_0 = 1 - A\log(1 + t'/\tau')$.● $- y = 10A$; Δ $- y = [G(t' = 600\text{ c}) - G_T/G(t' = 0) - G_T]$; ○ $- y = \log(10\tau')$. Here G_T is the dark conductance. The solid curves have been drawn arbitrarily. Film II, thickness $d = 1300$ Å.

relaxation, the time t' reached 10 days. We believe that the simplest explanation of the logarithmic nature of the relaxation is based on the existence of capture centers in classically inaccessible tunneling regions, so that a capture of carriers occurs through a tunneling process.[3,4] Adopting $l = 10$ Å as the mean free path of the carriers, we find an estimate $n = 10^{16}$ cm^{-3} of the carrier density in the illuminated state from the value of the conductance. An estimate of the carrier velocity, $v = 3\times10^7$ cm/s with $\tau_1' = 10^{-2}$ s, yields $\sigma_1' = (nv\tau_1')^{-1} \approx 3\times10^{-22}$ cm^2 as the cross section for the capture of carriers at the capture centers, in good agreement with estimates of the cross section for the capture of an electron accompanied by the emission of a photon.[2]

As was pointed out in Ref. 5, the number of free carriers in oxidized PbTe films increases during illumination as a result of a photodeionization of negatively charged acceptors formed by an oxygen impurity. We call these acceptors the "primary centers." As a result of the photodeionization of the acceptors, metastable secondary centers form; we call the process by which they return to their original state "recombination." This process may occur both through the capture of a conduction electron and through a transition of an electron from a nearest capture center. The secondary centers themselves can also serve as capture centers.

In the course of the experiments it was found that the observed relaxation at $t < 50$ K does not signify a recombination of secondary centers. At $T = 4.2$ K the application of light after relaxation (a second illumination) with $t' \leqslant 1$ h restored the original illuminated value of the conductance, G_0, with a deviation $(G_0 - G)/G_0 \lesssim 10^{-3}$ over a time $t'' \lesssim 5$ s (the time $t'' = t - 2400$ s in Fig. 1). The value of the derivative $\dot{G}(t = 1200)$ was restored simultaneously. Increasing t' to 3 days resulted in an increase in the required restoration time t'' to 50 s, but the initial value of the derivative of the second illumination, $\dot{G}_2 = \dot{G}(t'' = 0)$, was independent,

within an error $\sim 30\%$, of the duration of the relaxation. From this circumstance we can find an upper estimate of the cross section for the recombination of the secondary centers: $\sigma_2' < 10^{-30}$ cm^2 at $T = 4.2$ K. The time constant of the second illumination, defined as $\tau_2 = G_0/\dot{G}_2 \approx 0.1$ s, yields the value $\sigma_2 = (I\tau_2)^{-1} \approx 10^{-14}$ cm^2 for the cross section of the second photoionization, while for the first illumination we have $\sigma_1 = (I\tau_1)^{-1} \approx 0.3 \times 10^{-16}$ cm^2. The value of σ_1 is approximately equal to the typical photoionization cross section of deep donors,[2] while the number for σ_2 indicates a larger formation, of the nature of a hydrogen-like center.

Experiments including an intermediate annealing showed that the recombination of the secondary centers accelerates with increasing temperature. The first and second illuminations were carried out at $T = 4.2$ K, but in the middle of the relaxation interval the temperature was raised to $T = 20$–200 K for a time $t_{ann} \approx 1$ min. Increasing t_{ann} to 10 min caused essentially no changes in the results. At $T \geqslant 170$ K the initial rates of the first and second illuminations were the same, as can be seen in Fig. 3. At lower annealing temperatures, the initial rate of the second illumination increased with decreasing temperature in accordance with

$$\dot{G}_2 \propto \exp\left[(2E/\hbar\omega)\tanh(\hbar\omega/2kT)\right]$$

with the parameter values $\hbar\omega = 100$ K and $E = 380$ K. The thermal-activation dependence described here is typical of the reciprocal of the cross section for the radiationless capture of an electron to a deep level accompanied by the multiple emission of phonons, in a number $S \gg 1$ per recombination event.[2] Here $\hbar\omega$ is the energy of the phonon mode which is coupled most efficiently with the defect, and E is the height of

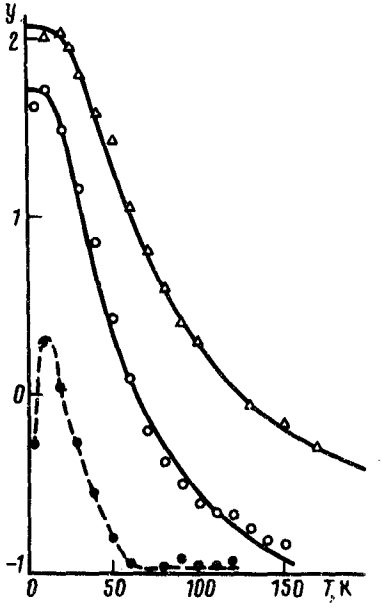

FIG. 3. Temperature dependence for film II: △: $y = \log \dot{G}_2$, T is the temperature of the intermediate annealing; the solid curve is calculated from the formula $y = 3.3\tanh(50/T) + \text{const}$. ○: $y = \log G(t = 1200\text{ s})$. ●: $y = \log \dot{G}_1(t = 0)$, T is the temperature of the first illumination. The solid lines show $y = 3.4\tanh(35/T) + \text{const}$. The dashed curve has been drawn arbitrarily. Here G is expressed in units of $M\Omega^{-1}$, and $\dot{G}$ in units of $M\Omega^{-1} \cdot s^{-1}$.

the activation barrier set up by the large local lattice deformation. The value which we found for $\hbar\omega$ by a fitting procedure lies between the values $\hbar\omega_{LO} = 160$ K and $\hbar\omega_{TO} = 50$ K, which have been found by neutron diffraction for longitudinal and transverse optical modes, respectively.[5]

The exceedingly small values $\sigma_2' \ll \sigma_1'$ in combination with the temperature dependence of $\dot{G}_2$ can be explained in the model of a pronounced lattice deformation. In this case there can be no capture of a carrier without a change in the configuration of atoms near the defect. The capture results from the presence of thermal or zero-point vibrations of the lattice and is itself accompanied by the emission of new phonons. Assuming the energy of the deep acceptor levels in PbTe to be ~ 0.1 eV, we find that $S = 10$ phonons are emitted per recombination event.

Also shown in Fig. 3 are data on the temperature dependence of the photoresponse. It is clear from a comparison with the curves in Fig. 2 that the increase in the effect with decreasing temperature cannot be explained in terms of a change in the relaxation. We also note that the photoionization cross section is essentially independent of the temperature for short-wave light.[2] We therefore suggest that the ratio of the number of conduction electrons to the number of secondary centers increases with decreasing temperature, in view of the decrease in the cross section for radiationless capture at defects in the sample.

To refine these suggestions, we carried out some experiments in which the first and second illuminations were carried out at different temperatures, T_1 and T_2, respectively. The temperature was changed (Fig. 1) at the middle of the relaxation interval. We note, for example, that the curve of the second illumination at $T_1 = 4.2$ K and $T_2 = 13.2$ K in Fig. 1 runs very close to the curve $T_1 = T_2 = 13.2$ K, which we have omitted. Similar comparisons of other curves show that the number of photoelectrons per event involving the formation of a secondary center does indeed depend on the temperature. Incidentally, we observed that illumination at $T = 50$ K generates capture centers with a larger photoionization cross section, as can be seen from the curve with $T_1 = 50$ K and $T_2 = 4.2$ K in Fig. 1. Furthermore, Fig. 1 clearly shows that the number of photoelectrons decreases significantly as the temperature is reduced below $T = 13.2$ K. This effect was observed in all the samples. It does not conform to the model of an effect of capture at capture centers. One could not expect the temperature to influence the carrier mobility in samples with a short carrier mean free path. The reasons for the nonmonotonic temperature dependence at such low temperatures remain unclean.

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