Recombination kinetic in GaP:Te investigated by phonon assisted tunneling in FIR fields

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We report for the first time on a direct measurement of the recombination kinetic in GaP highly doped by Te and the observation of long lasting storage of carriers in excited states. The measurements have been carried out within the temperature range between 20 K and 150 K. Tellurium donors have been ionized by 100 ns high power pulses of NH₃ FIR laser optically pumped by a TEA CO₂ laser with wavelengths, \( \lambda \), of 76, 90.5, 148, and 230 \( \mu \)m. The corresponding photon energies are much smaller than the binding energy of the impurities. Ionization is accomplished by phonon assisted tunneling in the electric field, \( E \), of the coherent radiation [1]. This has been proved by measurements of the photoconductive (PC) signal as a function of wavelength, intensity and temperature. The ionization probability, being independent on \( \lambda \), increases with the electric field like \( \exp(E^2/E_0^2) \) and corresponding tunneling times, determining \( E_0 \), decrease with temperature as 1/T.

The PC signal pulse shows at first a fast component which decays with the laser pulse due to the well known fast cascade capture of carriers in excited states of Coulomb centers. After the radiation has been ceased, however, the signal starts to rise again, assumes a maximum after about 1 \( \mu \)s (Fig. 1), and finally exponentially drops with a strongly temperature dependent time constant \( \tau \) varying from several microseconds to several milliseconds (Fig. 2). This temperature dependence can be fitted as \( 1/\tau = (1/\tau_0 \exp(-\Delta E/kT)+144) s^{-1} \) with \( \Delta E = 28 \) meV.

In addition, up-conversion of FIR radiation into a mid-IR radiation has been observed. A sample of bulk GaP:Te has been placed in front of a fast Ge:Cu extrinsic infrared detector, being sensitive to radiation of \( \lambda < 30 \mu m \). A KRS-5 window of the detector blocked totally the exciting laser beam. The irradiation of the sample by FIR radiation leads to a MIR luminescence signal.

We show that the introduction of an additional long living state, which has vanishingly small recombination probability to the ground state in the cascade process of recombination, describes the whole kinetic. Long living excited states have recently been anticipated for several shallow impurities in Ge and Si from cw microwave absorption measurements [2]. With the present investigation the long living state can be identified as the valley split 1s(E) level of Te donors in GaP.

The inset (bottom, left) of Fig. 2 shows the structure of the cell's back bottom of the conduction band and the levels of the ground and lowest excited states of Te. After the rapid cascade capture carriers are accumulated in the 1s(E) state which has a very long life time of the about 10 ms.
for direct transitions into the ground state. By thermal activation carriers are re-injected into the densely lying Coulombic states close to the band edge. By this the stored carriers are introduced in the fast recombination channel. The recombination of carriers from 1s(E) state takes place by thermal excitation into the next higher s-state 2s(A) which lies 28 meV above 1s(E) state. The 2s(A) state is close to several p-states, therefore, by the exchange between these states due to absorption and emission of acoustic phonons, radiative recombination to the ground state is possible. It explains the observed IR luminescence. Electrons are accumulated in the lowest excited s-state because the energy separation between that state and the ground state is much bigger than the largest acoustic phonon energy (31.5 meV), but still smaller than the optical phonon energy. This kinetic model is sketched in an inset (top, right) of Fig. 2 where $\tau_{EA}$, $\tau_{2A}$, and $\tau_{TE}$ indicate the time constants and $e_{2A}$ and $e_{TE}$ the probabilities of reverse processes, respectively.

![Graph showing the relationship between temperature and recombination rate](image)

It can be shown that after irradiation the solution of the corresponding rate equations is given by:

$$n_2(t) = \frac{e_{TE}e_{2E}}{(\tau_{2E}^{-1} - \tau_{1E}^{-1})} \left[ \exp \left( \frac{(t-t_0)}{\tau_{d1}} \right) - \exp \left( \frac{(t-t_0)}{\tau_{d2}} \right) \right]$$

(1)

with dynamic relaxation times $\tau_{d1}$ and $\tau_{d2}$:

$$\frac{1}{\tau_{d1}} = \frac{1}{\tau_{2A}} + \frac{1}{\tau_{2E}} + \frac{e_{2A}}{(\tau_{2A} + \tau_{2E})}$$

and

$$\frac{1}{\tau_{d2}} = \frac{e_{2E}}{(\tau_{2A} + \tau_{2E})} + \frac{1}{\tau_{EA}}$$

where $n_2$ is the density of electrons in the 2s(A) state, which reflects the density of non-equilibrium electrons in the conduction band. It is seen that (1) describes all experimental observations if $\tau_{2E} < \tau_{2A} < \tau_{EA}$. The two dynamic relaxation times differ at least by two orders of magnitude and, in fact, a one parameter fitting procedure was sufficient for the whole temperature range. Full lines in Fig. 1 and 2 show the result of the fit with time constants $\tau_{2E} = 10^{-7}$ s, $\tau_{2A} = 5 \times 10^{-7}$ s and $\tau_{EA} = 0.7 \times 10^{-2}$ s.

In summary, optical transitions have been detected by the observation of mid-infrared luminescence. The high excess carrier density in the excited impurity state may be of interest for the development of an IR semiconductor impurity laser. The use of FIR laser pulses for carriers excitation is not stringent. Indeed, only the electric field strength of FIR radiation has been utilized to excite free carriers, but the last can be obtained by applying short electric pulses.

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