

Inter-valence-band scattering and cooling of hot holes in *p*-type germanium studied by picosecond infrared pulses

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The transient absorption from the heavy-hole band to the light-hole band of *p*-type germanium is investigated at a wavelength of 10 μm . A nonequilibrium carrier distribution is generated by an intense pump pulse and the resulting change of absorption is monitored. A strong bleaching followed by an absorption increase is observed depending upon the excitation intensity and the initial carrier temperature. The inter-valence-band scattering of the excited holes via optical phonons occurs on a subpicosecond time scale, whereas the subsequent cooling continues for tens of picoseconds.

The infrared spectrum of *p*-type germanium in the wavelength range from 3 to 30 μm represents the prototype of inter-valence-band absorption of free holes in semiconductors. The absorption band found around 10 μm is due to transitions from the heavy-hole band to the light-hole band.¹ The stationary spectra were well explained by the structure of the valence band taking into account the nonparabolicity and the warping of the different bands.^{2,3}

A strong bleaching of the absorption band at 10 μm was observed after excitation with intense nanosecond pulses from CO₂ lasers.⁴⁻⁸ For hole concentrations of $N_h \lesssim 10^{16} \text{ cm}^{-3}$ saturation intensities in the range of several MW/cm² were reported for a sample temperature of 300 K. The bleaching of the transition has been analyzed considering an ensemble of inhomogeneously broadened two-level systems.⁹ The decrease of absorption is attributed to the depletion of the ground state in the two-level systems by the intense laser excitation. The coupling to optical phonons was identified as the main relaxation mechanism of the excited holes.

Carrier-carrier and carrier-phonon scattering occur on a time scale much shorter than 1 ns. As a result, experiments with nanosecond time resolution give no information on the relaxation of hot holes immediately after inter-valence-band excitation. In this paper, we present direct measurement of the inter-valence-band scattering and the cooling of hot holes in *p*-type germanium. The nonlinear change of absorption at a wavelength of 10 μm is monitored by experiments with a temporal resolution of 1 ps. Data are presented for a wide range of sample temperatures from 30 to 300 K. The experimental results are analyzed by detailed model calculations of hot hole relaxation. Our results suggest a reinterpretation of the previous nanosecond measurements.

In our experiments, a first intense infrared pulse excites part of the holes from the heavy-hole band to the light-hole band. The resulting change of absorption is monitored by a weak probe pulse at the same wavelength. The transient absorption is measured as a function of the delay time between excitation and probe pulses to determine the relaxation kinetics. The carrier density is constant in this type of experiment; i.e., the infrared excitation pulse

redistributes the holes present by doping. In this paper, we focus on data for a wavelength of 10 μm . This spectral position was chosen to facilitate comparison of our picosecond measurements with previous results obtained with nanosecond excitation by CO₂ lasers.

Single infrared pulses with a duration of 2 ps are generated by parametric frequency conversion.¹⁰ The output of a mode-locked Nd:glass laser and of a traveling-wave dye laser working in the near infrared are mixed in a Ag-GaS₂ crystal to generate the difference frequency. The bandwidth and the energy of the pulses at 10 μm have values of 15 cm⁻¹ and 5 μJ , respectively. A gallium-doped germanium crystal with a thickness of 0.04 cm is investigated here. The sample has a resistivity of 0.07 Ωcm corresponding to a hole density of approximately $N_h = 10^{17} \text{ cm}^{-3}$.

In a first series of measurements, the temporal behavior of the absorption from the heavy-hole band to the light-hole band is studied at different lattice temperatures T_L of the sample. The experimental results are presented in Fig. 1, where the change of absorption $\Delta A = -\ln(T/T_0)$ is plotted versus the delay time between excitation and probe pulses (solid circles). T_0 and T represent, respectively, the transmission of the sample prior to and after excitation. The peak intensity of the pump pulse has a value of 30 MW/cm². At room temperature [Fig. 1(a)], a decrease of the inter-valence-band absorption is found, which rises rapidly and recovers within 10 ps. A completely different behavior is observed at $T_L = 80 \text{ K}$ as shown in Fig. 1(b). Here the initial fast bleaching is followed by a strong increase of absorption, which decays on a time scale of 30 ps. The enhanced absorption is even more pronounced at $T_L = 30 \text{ K}$ [Fig. 1(c)]; it relaxes within 100 ps after excitation.

The strength of the positive and negative components of the absorption change ΔA depends on the excitation intensity. In Fig. 2, data for three different peak intensities of the pump pulses are presented for a lattice temperature of $T_L = 80 \text{ K}$. The fast bleaching component is strongly reduced for smaller intensities, whereas the peak value of the enhanced absorption decreases by only a factor of 2 for an attenuation of the pump pulse by a factor of 30 (in Fig. 2 the data are normalized to the peak of the enhanced

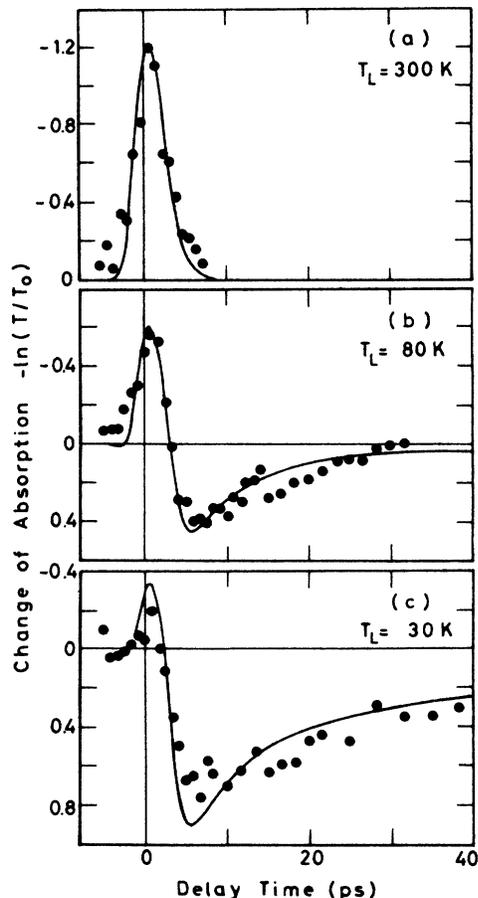


FIG. 1. Transient change of the interband absorption of holes at a wavelength of $10\ \mu\text{m}$. The absorption change $\Delta A = -\ln(T/T_0)$ is plotted vs the delay time between pump and probe pulses (T_0, T : transmission before and after excitation of the sample). Data for lattice temperatures T_L of (a) $T_L = 300\ \text{K}$, (b) $T_L = 80\ \text{K}$, and (c) $T_L = 30\ \text{K}$ are presented (solid circles). The solid lines are calculated.

absorption). The decay time of the absorption increase varies only slightly with intensity.

Additional measurements were performed with a germanium crystal with a lower hole density of $N_h = 10^{16}\ \text{cm}^{-3}$; i.e., with a sample of a doping level typical for most of the previous nanosecond experiments. In this sample, similar behavior of the transient absorption and relaxation of hot holes is observed.

We now consider the mechanisms responsible for the absorption changes found in our experiments. Two effects changing the infrared absorption on a picosecond time scale have to be considered: (i) The excitation pulse drives part of the holes from the heavy-hole band to the light-hole band leading to a decrease of carrier density in the initial states of the optical transition. The depletion of the heavy-hole band results in an absorption decrease. (ii) The excited holes return to the heavy-hole band with excess energy supplied by the absorbed infrared photons. Thus, inter-valence-band scattering leads to the formation of a hot carrier distribution in the heavy-hole band. The high transient temperature of the heavy holes and the cor-

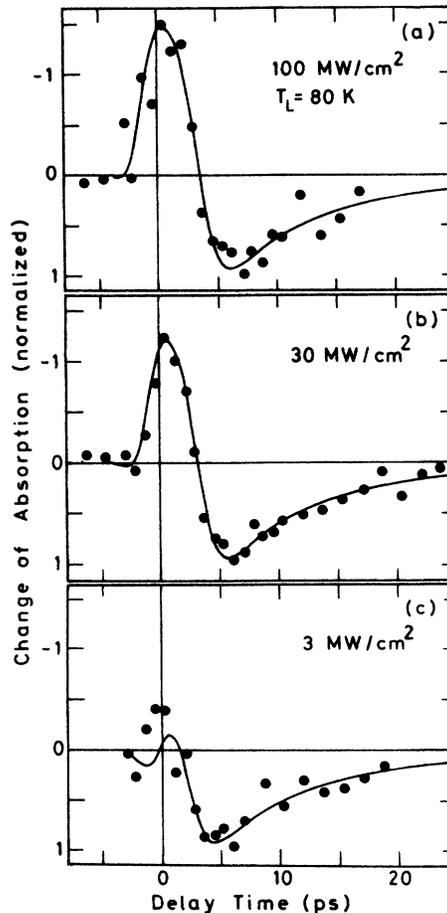


FIG. 2. Time-dependent change of absorption at $10\ \mu\text{m}$ for three different peak intensities of the excitation pulses. The bleaching at early delay times markedly decreases with smaller intensity, whereas the subsequent absorption increase shows a much weaker intensity dependence.

responding change of the Fermi distribution modify the carrier density in that interval of k space which is connected with the absorption of infrared photons at $10\ \mu\text{m}$. Consequently, the absorption of the sample changes. The sign of the absorption change critically depends on the initial temperature of the holes, i.e., on the lattice temperature T_L .

To determine the changes in the absorption coefficient quantitatively, we have performed model calculations following the formalism developed by Kane.³ The nonparabolic and nonspherical structure of the valence bands is treated by $k \times p$ perturbation theory. The absorption coefficient is calculated from the k -dependent dipole matrix element of the heavy-hole-to-light-hole transition taking into account the carrier distribution in the heavy-hole band. The result of a hole density of $N_h = 10^{17}\ \text{cm}^{-3}$ is depicted in Fig. 3 (solid line). Starting at low carrier temperatures T_c , where the states at small wave vectors k are predominantly populated, a rise of the carrier temperature is connected to an increase of population in the relevant states at higher k values, resulting in a stronger absorption at $10\ \mu\text{m}$ (see Fig. 3 inset, distribution func-

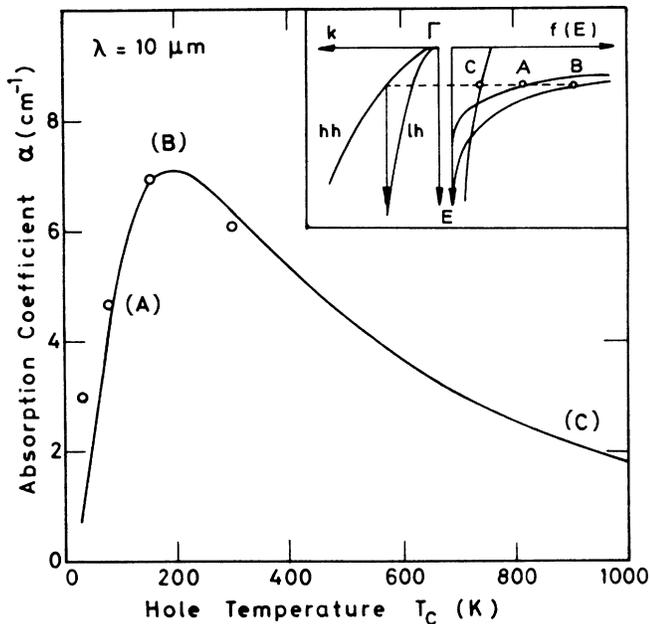


FIG. 3. Calculated absorption coefficient at a wavelength of $10 \mu\text{m}$ as a function of the temperature T_c of heavy holes (solid line, hole density $N_h = 10^{17} \text{ cm}^{-3}$). Open circles: Experimental values of the absorption coefficient for various sample temperatures ($T_L = T_c$). Inset: Schematic of interband transitions from the heavy-hole (hh) to the light-hole (lh) band. The distribution functions for three T_c values at A, B, and C are depicted.

tions A and B). For a higher initial T_c , a substantial population of the states relevant for absorption exists. Additional heating of the carriers now reduces the absorption coefficient since—for a constant density of holes—the strong thermal broadening of the distribution function leads to a decrease of population density (see Fig. 3 inset, distribution functions B and C). The calculated curve is in good agreement with our steady-state data in the range from 80 to 300 K, where lattice and carrier temperature are the same (open circles).¹¹

The time dependence of the absorption changes following picosecond inter-valence-band excitation is calculated from a model of the relaxation processes of hot holes. At a hole density of $N_h \approx 10^{17} \text{ cm}^{-3}$, the carrier-carrier scattering time lies in the subpicosecond range.¹² The holes in the different valence bands relax to Fermi distributions during picosecond excitation. The interaction with optical phonons via the deformation potential represents the main mechanism of interband scattering and of intraband cooling of the thermalized holes.¹³ The corresponding coupling constant is identical for intra- and interband scattering and has a value of $D_k = 9.0 \times 10^8 \text{ eV/cm}$.¹⁴ In the calculation, we start with two separate Fermi levels and temperatures for the heavy and light holes. The differential equations for the time-dependent carrier densities and temperatures after picosecond interband excitation are solved numerically for the two bands. The kinetics of the absorption change at $10 \mu\text{m}$ is calculated from the distribution functions according to Kane's model. Finally, the calculated change of absorption is

convoluted with the time envelope of the probe pulse.

The following relaxation behavior is obtained from theory: (i) Inter-valence-band scattering of the optically excited holes occurs on a subpicosecond time scale due to the fast emission of optical phonons. For a pump intensity of $I = 30 \text{ MW/cm}^2$ in our experiments, the density of absorbed photons is close to the total concentration $N_h = 10^{17} \text{ cm}^{-3}$ of holes. Even for this strong excitation, the transient excess density of light holes reaches a maximum value of less than $N_h/10$. The excess population of the light-hole band follows in time the envelope of the excitation pulse and is negligibly small at delay times longer than 3 ps. After that time, the carrier system is characterized by a single Fermi level and temperature T_c . (ii) Due to the rapid interband scattering, the heavy holes reach a high transient temperature T_c of up to 900 K ($I = 30 \text{ MW/cm}^2$). The maximum T_c occurs at a delay time of approximately 1 ps. The subsequent cooling of the hole distribution by phonon emission continues for several tens of picoseconds. For a low initial temperature, $T_c = T_L$, of the carriers, the relaxation via emission of optical phonons becomes less efficient at late delay times, where the hole temperature has been reduced substantially.

The calculated kinetics of the absorption change is plotted in Figs. 1 and 2 (solid lines). The numerical results are in good agreement with the experimental data. The fast bleaching at room temperature [Fig. 1(a)] is mainly due to the rise of the carrier temperature T_c (cf. Fig. 3). The depletion of the heavy-hole band makes only a small contribution. At lower lattice temperatures $T_L \lesssim 80 \text{ K}$ [see Figs. 1(b), 1(c), and 2], the transient rise and decay of T_c leads to a complex kinetics of the absorption change ΔA : At early delay times, where T_c is very high, the absorption coefficient α_h is even less (area C of Fig. 3) than the relatively small initial value of α_h and a bleaching is observed. With decreasing carrier temperature, the transient α_h reaches values higher (area B in Fig. 3) than the original absorption giving rise to a positive ΔA .

The strength of the bleaching signal at early delay times is a sensitive probe of the maximum carrier temperature T_c . For smaller intensities of the pump pulse, the fraction of excited holes and, as a result, the maximum T_c decreases. The data in Fig. 2 reveal the corresponding strong reduction of the bleaching component, whereas the subsequent absorption increase occurring during the cooling process at lower T_c remains unaffected.

The present results should be compared to previous nanosecond measurements, which were, in most cases, performed at room temperature. Our data demonstrate that the picosecond absorption changes are governed by the time-dependent carrier temperature. A rise in the temperature of heavy holes from 300 K to higher values of T_c results in a decrease of absorption, as a consequence of the change of the distribution function (cf. Fig. 3). Even after intense excitation, the transient excess density of light holes is negligible for delay times longer than 3 ps; i.e., a substantial nonequilibrium population in the light-hole band on a longer time scale does not exist. This finding suggests that the bleaching observed with nanosecond pulses of high intensity is mainly due to the heating of the carrier system, but *not* due to the generated

difference of population in the heavy- and light-hole band.

In summary, we have presented the first direct measurements of the relaxation of hot holes in *p*-type germanium after picosecond infrared excitation. The subpicosecond interband scattering by emission of optical phonons is followed by the cooling of heavy holes within several tens of picoseconds. Bleaching, as well as a tran-

sient absorption increase, is detected depending on the excitation intensity and the initial carrier temperature. The theoretical analysis shows that the absorption changes are determined by the time-dependent carrier temperature. Picosecond infrared spectroscopy provides very direct information on the relaxation of hot holes in semiconductors.

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