Picosecond Capture of Photoexcited Holes by Shallow Acceptors in p-Type GaAs

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Ultrafast recombination of holes with shallow acceptors in a III-V semiconductor is directly observed for the first time, by means of picosecond infrared spectroscopy. Neutral impurities in p-doped GaAs at low temperature are photoionized by picosecond infrared excitation. The recombination of free holes with negatively charged acceptors—monitored via absorption changes below the band edge—occurs on a time scale of several tens of picoseconds, following a nonexponential kinetics. Emission of longitudinal-optical phonons by the free holes is found to be the dominant mechanism of recombination.

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The energy levels of shallow impurities in extrinsic semiconductors represent localized electronic states which strongly affect the optical and electrical properties of the material. Dipole-allowed transitions between the ground state of impurities and delocalized states in the valence and conduction bands result in distinct absorption and emission bands [1]. For charge transport at high electric fields, repeated scattering of carriers between continuum states and the excited levels of the impurities, i.e., carrier trapping and impurity ionization, reduces the conductivity of the material. Those processes are particularly relevant at low temperatures and high doping densities where a certain fraction of impurities is ionized [2].

In the early cascade-capture model, carrier trapping is described as emission of a sequence of single acoustic phonons, followed by a final relaxation to the impurity ground state [3]. Refined theoretical treatments have been developed to account for multiple scattering and have calculated cross sections of carrier capture [2]. More recently, Monte Carlo techniques have been used to simulate the kinetics of charge transport [2,4]. Extensive experimental work has concentrated on stationary transport or electrical noise measurements giving capture cross sections for shallow donors and acceptors in silicon and germanium [5]. In contrast, very limited information exists on the *microscopic dynamics* of carrier capture. Nanosecond trapping times have been deduced from time-resolved transport studies on n-type germanium [6] and from the photo-Hall effect of p-type silicon [7]. In GaAs, time-resolved studies of impurity related luminescence report electron and hole capture on a time scale between 10 and 500 ns [8]. The observed relaxation rates are mainly determined by the interaction between free carriers of low kinetic energy and acoustic phonons [2]. In GaAs and other III-V semiconductors, the interaction with optical phonons is much stronger than the acoustic deformation potential. Thus enhanced capture rates should occur if electrons and holes have sufficient energy to emit longitudinal (LO) or transversal (TO) optical phonons. Furthermore, the large energy of the optical phonons compared to acoustic phonons allows the direct population of the ground state of a shallow impurity by emission of a single optical phonon if the phonon energy is higher than the ionization energy E_{acc} of the impurity. This process facilitates the capture of high energy, i.e., hot carriers. Until now, an experimental observation and quantitative characterization of hot carrier capture in shallow impurities by emission of optical phonons is still lacking. For a direct measurement of the relaxation dynamics, a high time resolution in the picosecond or subpicosecond regime is required, now available by ultrashort laser pulses.

In this Letter, we present the first direct evidence of ultrafast hole capture by emission of LO phonons in GaAs. The transient deionization absorption band of negatively charged acceptors is monitored with picosecond near-infrared pulses, revealing a nonexponential recombination dynamics of photoexcited holes on a time scale of several 10^{-11} s. Emission of single LO phonons by the free carriers is identified as the main relaxation channel, directly populating the ground state of the ionized acceptors. For a density $N_{A^-}=10^{17}$ cm^{-3} of generated ionized acceptors, our new data give a capture rate of $W_{\mathrm{trap}}=1.5\times10^{11}$ s^{-1} corresponding to a trapping cross section of 1.5×10^{-13} cm^2 for zinc-doped GaAs.

GaAs crystals (thickness 10 μm) with an acceptor concentration of 7×10^{17} cm^{-3} were investigated at a lattice temperature of $T_L=10$ K. Picosecond infrared pulses of 2-ps duration were produced by parametric difference frequency mixing in the wavelength range from 3.5 μm (350 meV) to 12 μm (105 meV) [9]. These pulses generate free holes in the GaAs sample. Tunable probe pulses of a duration of 4 ps (spectral bandwidth 5 nm) were derived from a picosecond white light continuum; they monitor transient absorption changes in the near infrared around 850 nm (1.5 eV).

Our novel experimental technique is explained with the help of Fig. 1. In p-type GaAs, the holes are bound to the Zn acceptors at low lattice temperatures T_L where kT_L (k is the Boltzmann constant) is much smaller than the ionization energy $E_{\mathrm{acc}}=27$ meV [10]. The infrared absorption plotted in Fig. 1(a) for $T_L=10$ K is due to transitions of holes from the ground state of the neutral acceptor to the light-hole band (photon energies below 350 meV) and to the split-off band (above 350 meV). The absorption edge of our sample connected with transi-

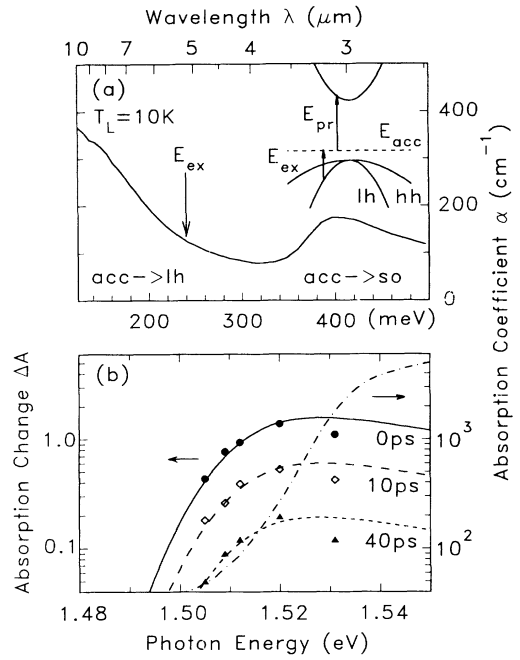

FIG. 1. (a) Steady-state absorption spectrum of p-type GaAs between 2.5 and 10 μm. The absorption coefficient of a Zn-doped sample (acceptor concentration $N_A = 7\times10^{17}$ cm^{-3}) is plotted vs photon energy for a lattice temperature of $T_L = 10$ K (solid line). The arrow at $E_{ex} = 240$ meV marks the photon energy of the picosecond excitation pulses. The electronic transitions relevant for the picosecond experiments are depicted in the inset. (b) Transient deionization band ΔA for delay times of 0, 10, and 40 ps, as derived from the picosecond measurements (symbols). The solid and the dashed lines give the calculated deionization bands (ordinate on the right-hand side). In addition, the absorption edge of the p-type GaAs sample at $T_L = 10$ K is shown (dash-dotted line).

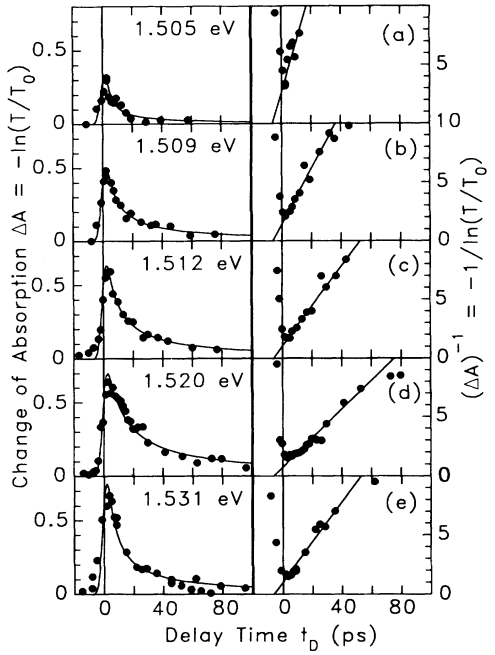

FIG. 2. Transient interband absorption of negatively charged acceptors observed after picosecond infrared excitation at $E_{ex} = 240$ meV. On the left-hand side, the increase of absorption $\Delta A = -\ln(T/T_0)$ is plotted vs delay time t_D for probe energies E_{pr} of (a) 1.505 eV, (b) 1.509 eV, (c) 1.512 eV, (d) 1.520 eV, and (e) 1.531 eV (T and T_0 are the transmission of the sample with and without excitation). On the right-hand side, the inverse signal $1/\Delta A$ is plotted vs t_D. Here, one finds a linear time dependence with a slope depending on the specific E_{pr}. The solid lines are calculated from a theoretical model.

tions from the valence to the conduction band is shown in Fig. 1(b) by the dash-dotted line. Of importance in the present study is an additional absorption band around 1.510 eV which is observed when part of the acceptors is ionized. Transitions from the ground state of the negatively charged acceptors to the conduction band give rise to the acceptor deionization band [1]; its strength is directly proportional to the density N_A^- of ionized acceptors [solid and dashed lines in Fig. 1(b)]. In our picosecond measurements, initially neutral acceptors are ionized by intense infrared excitation ($E_{ex} = 240$ meV) to the light-hole band and the resulting transient deionization band is monitored by tunable probe pulses (E_{pr}) of variable time delay. The enhanced absorption is governed by the momentary density of ionized acceptors which is identical to the density of holes in continuum states. Thus the rise and decay of the transient deionization band directly reveals, respectively, the depopulation and repopulation dynamics of the acceptor ground state.

On the left-hand side of Fig. 2, the induced absorption $\Delta A = -\ln(T/T_0)$ observed after excitation at $E_{ex} = 240$ meV is plotted versus delay time for five photon energies E_{pr} of the probe pulses (T and T_0 are the transmission of the sample with and without excitation). The transient data points rise within the time resolution of the experiment and subsequently decay on a time scale of 100 ps following a nonexponential kinetics. The maximum density of free holes $p_0 \simeq 10^{17}$ cm^{-3} is estimated from the maximum value of ΔA around delay zero and from the cross section $\sigma_{deion}(E_{pr})$ of the deionization band at the different values of E_{pr}. The latter was determined in an independent measurement of the radiative lifetimes of the conduction band to acceptor luminescence [11].

On the right-hand side of Fig. 2, our data are replotted as $1/\Delta A$ vs t_D. Within the experimental accuracy, the relaxation dynamics follows a linear time dependence (solid lines), with a slope depending on the spectral position E_{pr}. The different straight lines intersect the abscissa at a common value of $t_D = -6$ ps. We stress the linear relationship between $1/\Delta A$ and t_D which will be discussed below.

The transient absorption spectra of the ionized acceptors are derived from our detailed time-resolved data. In Fig. 1(b), the change of absorption $\Delta A(E_{pr})$ is plotted versus photon energy E_{pr} for several fixed delay times

(circles, 0 ps; diamonds, 10 ps; triangles, 40 ps). The solid line which is in good agreement with the experimental points, represents the deionization band calculated for a value of $N_A^- = p_0 = 10^{17}$ cm^{-3} (ordinate scale on the right-hand side). The transient absorption band decays without changing its shape (dashed lines); i.e., the enhanced absorption at different photon energies reveals the same relaxation behavior of the photoexcited carriers.

Next, we discuss the carrier relaxation processes occurring after photoionization of the initially neutral acceptors. Absorption of infrared photons of 240 meV promotes holes to the light-hole band and generates negatively charge acceptors seen by the transient absorption studied in our measurements [12]. Thermalization and inter-valence-band scattering of the free holes lead to the rapid formation of a hot quasiequilibrium distribution in the heavy-hole continuum states [13]. This initial relaxation is dominated by carrier-carrier scattering and by interaction with optical phonons, both proceeding on a subpicosecond time scale [14], i.e., within the time resolution of our present experiment of 1 ps. The quasiequilibrium distribution of free holes continues to cool rapidly by transferring energy to the lattice via emission of optical phonons. For excitation densities around 10^{17} cm^{-3}, high-energy-loss rates were reported, leading to a fast decrease of the carrier temperature from several hundred kelvin to approximately 50 K within the first few picoseconds after excitation [15]. The rapid cooling is followed by recombination of holes in the continuum states with the negatively charged impurities, resulting in the repopulation of the acceptor ground state. This final relaxation process is directly observed in our experiments via the disappearance of the transient deionization band.

Several capture processes have to be considered. A quantitative estimate for a hole density of $p_0 = 10^{17}$ cm^{-3} shows that the capture rates due to radiative recombination by emission of an infrared photon or due to Auger recombination of hole and ionized acceptor are several orders of magnitude smaller than what is found in the present experiments [16]. Cascade emission of acoustic phonons, and the inverse process of phonon absorption are important for carrier capture and reionization of the closely spaced excited states of a shallow impurity. However, repopulation of the impurity ground state via acoustic phonons occurs with a very small probability since the energy separation of the low-lying acceptor states is larger than the acoustic phonon energy of a few meV [3]. For similar reasons, capture by carrier-carrier scattering can be neglected.

We now consider hole capture by emission of optical phonons. The ionization energy of the Zn acceptor of 27 meV is smaller than the energy of the LO and TO phonons of $\hbar\omega_{LO} = 37$ meV and $\hbar\omega_{TO} = 34$ meV, respectively. Holes populating continuum states which are one phonon energy above the acceptor ground state can be trapped by emission of a single optical phonon. The extremely low stationary population N_q of the optical phonon branches at a lattice temperature $T_L = 10$ K and the small phonon excess population transiently generated by cooling of hot holes ($N_q \ll 0.01$) result in a negligible probability of acceptor reionization by phonon absorption. The capture rate depends on the polar-optical coupling and the optical deformation potential, the density of ionized acceptors, and the transient population of continuum states from where optical phonon emission is possible. For a quantitative analysis, we first calculate the corresponding matrix elements between the continuum and the localized acceptor ground state [17,18]. The average trapping rate W_{trap} is obtained by (i) summing up the scattering probabilities for all phonon wave vectors q, and (ii) integrating over the (Maxwellian) distribution function of the free holes. W_{trap} can be written as $W_{trap} = C_{trap} N_A^-$, with the trapping parameter C_{trap} and the density of ionized acceptors N_A^-. The parameter C_{trap} depends on the coupling matrix elements, the wave function of the impurity ground state [17], the ionization energy $E_{acc} = 27$ meV [10], and the temperature T_C of the free holes. T_C governs the population of the relevant valence-band states. For a hole temperature of $T_C = 50$ K, one calculates $C_{trap} \simeq 2 \times 10^{-6}$ cm^3/s. The quantitative evaluation demonstrates that LO phonon emission due to polar optical coupling makes the main contribution to the overall capture rate. The emission of LO and TO phonons via the optical deformation potential contributes approximately 10% to the total value of C_{trap}.

In the present model, we consider the picosecond kinetics of hole capture to the ground state of the acceptors. A more detailed insight into hole relaxation at very early times, i.e., femtosecond carrier-carrier scattering and subpicosecond cooling of the hot holes, may be gained by Monte Carlo simulations of the carrier dynamics.

As pointed out above, the time-dependent density of free holes, $p(t)$, is identical to the concentration of ionized acceptors, $N_A^-(t)$. Thus $p(t)$ obeys the equation

$$\frac{dp(t)}{dt} = -C_{trap} p(t) N_A^-(t) = -C_{trap} p(t)^2 , \qquad (1)$$

which is solved by the expression $p(t) = (1/p_0 + C_{trap} t)^{-1}$ (p_0 is the initial density of holes). Correspondingly, the inverse absorption change

$$1/\Delta A(t) = [N_A^-(t) \sigma_{deion}(E_{pr}) l]^{-1}$$

is given by

$$\frac{1}{\Delta A(t)} = \frac{1}{p_0 \sigma_{deion}(E_{pr}) l} + \frac{C_{trap}}{\sigma_{deion}(E_{pr}) l} t . \qquad (2)$$

Equation (2) shows a linear time dependence of $1/\Delta A$ with a slope determined by the trapping parameter C_{trap} and the absorption cross section $\sigma_{deion}(E_{pr})$ of the deionization band at the specific photon energy E_{pr} (l is the sample thickness). As a result, the *same* carrier dynamics gives rise to a different time dependence of $1/\Delta A$ at

various photon energies E_{pr}. The time behavior calculated from Eqs. (1) and (2) is borne out by the experimental data of Fig. 2 [19]: (i) The slopes of the measured $1/\Delta A(t)$ curves are proportional to $1/\sigma_{deion}(E_{pr})$ which varies with E_{pr} according to Fig. 1(b). (ii) Extrapolation of the different kinetics to $1/\Delta A(t_0)=0$ gives a common value of $t_0=-(C_{trap}p_0)^{-1}=-6$ ps for *all* spectral positions; i.e., a single C_{trap} accounts for the whole set of data. With the experimental number of $p_0=10^{17}$ cm^{-3}, we derive a trapping constant of $C_{trap}=1.5\pm0.5\times10^{-6}$ cm^3/s from the time resolved data. The solid lines in Fig. 2 which account quantitatively for the data are calculated with this trapping constant and the known absorption cross sections $\sigma_{deion}(E_{pr})$. The good agreement of the trapping parameter C_{trap} determined from the experimental results with the number calculated above for LO phonon scattering gives convincing evidence that *the ultrafast capture of holes observed in our experiments is due to emission of single LO phonons.*

In conclusion, the results presented here give the first direct evidence of ultrafast hole capture by shallow acceptors in GaAs. Our spectrally and temporally resolved measurements with picosecond infrared pulses reveal a ground-state repopulation of the ionized acceptors on a time scale of 10^{-11} s. Our results demonstrate that the emission of single LO phonons represents the dominant mechanism of hole capture. These trapping phenomena are expected to be important for hot hole transport and for the kinetics of band-to-band and band-to-acceptor luminescence in III-V semiconductors.

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