Ultrafast thermalization of nonequilibrium holes in *p*-type germanium studied by femtosecond infrared spectroscopy

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(Received 29 December 1993)

Relaxation of holes photoexcited to the splitoff valence band by femtosecond pulses in the mid-infrared is directly monitored via the transient inter-valence-band absorption. Two thermalization processes are distinguished. The excited carriers undergo inter-valence-band scattering within 100 fs and thermalize with time constants around 700 fs. In contrast, equilibration of unexcited holes occurs within 100 fs. Theoretical calculations show that the dynamically screened Coulomb interaction among the holes and emission of optical phonons represent the main scattering mechanisms.

The nonequilibrium dynamics of carriers on the subpicosecond time scale is of fundamental importance for the electronic and optical properties of semiconductors. Optical spectroscopy using femtosecond laser pulses allows the creation of well-defined nonequilibrium distributions of electrons and holes and provides direct information on the elementary scattering processes by which the carriers thermalize, i.e., relax towards quasiequilibrium distributions.[1-8] In most cases, thermalization has been studied with photoexcited electron-hole plasmas in both bulk material and quasi-two-dimensional quantum-well systems.[1-5] Such experiments reveal the combined relaxation of electrons and holes and their mutual interaction. Specific information on electron-electron scattering and on the interaction of electrons and optical phonons has been obtained from measurements of band-to-acceptor luminescence.[9-11]

Much less information exists on the ultrafast dynamics of holes. Recently, femtosecond luminescence experiments with *n*-doped bulk GaAs and GaAs/AlGaAs quantum wells have been reported where the recombination of photoexcited holes with electrons present by doping allowed a study of the hole dynamics.[6-8] The onset of emission resonant to the band gap was monitored with 100-fs time resolution. In Refs. 6 and 7, initial equilibration times of several hundreds of femtoseconds were derived from data taken at lattice temperatures $T_L \leq 77$ K. Scattering of holes with the electron plasma was considered to be the dominant mechanism of thermalization. In contrast, the room-temperature measurements of Ref. 8 were interpreted in terms of a much faster equilibration and hole-electron scattering was assumed to be of minor importance.

The investigation of pure hole plasmas in *p*-type materials avoids the problem of hole-electron interaction and promises the direct measurement of ultrafast hole relaxation phenomena. In this paper, we present the time-resolved observation of ultrafast thermalization in a hole plasma. *p*-type germanium is studied as a prototype material with a valence-band structure similar to GaAs and other III-V compounds. Transient changes of the inter-valence-band absorption are investigated in spectrally and temporally resolved measurements with femtosecond pulses in the mid-infrared region. We demonstrate that thermalization of holes excited to the splitoff band proceeds with time constants around 700 fs by inelastic carrier-carrier scattering, transferring the excess energy to the cold plasma of unexcited holes. Equilibration of energy among the unexcited carriers occurs on an even faster time scale of less than 100 fs.

A gallium-doped germanium crystal with an acceptor concentration of 3×10^{17} cm^{-3} (sample thickness 0.02 cm) is studied in the present experiments. The infrared excitation pulse promotes holes to the splitoff (SO) band (spin-orbit splitting $E_{SO}=290$ meV) as depicted schematically in Fig. 1(a). The resulting change of the heavy-hole (HH) to SO absorption is monitored by weak delayed pulses in spectrally and temporally resolved measurements. Synchronized pump and probe pulses of 250-fs duration, which are independently tunable in the wavelength range from 2.7 (460 meV) to 5.0 μm (250 meV), are generated by parametric difference frequency mixing in two $LiIO_3$ crystals.[12,13] The time-integrated cross correlation of pump and probe pulses shown in Fig. 2(a) was measured with the help of the interband bleaching of a lead salt semiconductor. This instantaneous response serves for calibration of delay zero in the time-resolved experiments.[13] The energy of pump and probe has a value of 10 nJ and 500 pJ, respectively. The excitation density estimated from the incoming flux of infrared photons and from the absorption of the sample lies between 3×10^{15} and 10^{16} cm^{-3}, i.e., a small fraction of 1–3 % of the total hole concentration is excited to the SO band.

The absorption spectrum of *p*-type germanium due to inter-valence-band transitions from the HH to the SO band is plotted in Fig. 1(b) for lattice temperatures of $T_L=10$ and 80 K.[14,15] In the femtosecond experiments, transient changes of this absorption are studied with excitation (E_{ex}) and probe (E_{pr}) pulses between 400 and 445 meV as indicated by the arrows in Fig. 1(b). Time-resolved data for the four probe energies are presented in Figs. 2(b)–2(e), where the change of absorption ΔA is plotted versus delay time (points; lattice temperature $T_L=10$ K). At all probe energies, we observe a transient *increase* of absorption ($\Delta A>0$) that rises with a distinct delay relative to the instantaneous response in Fig. 2(a).

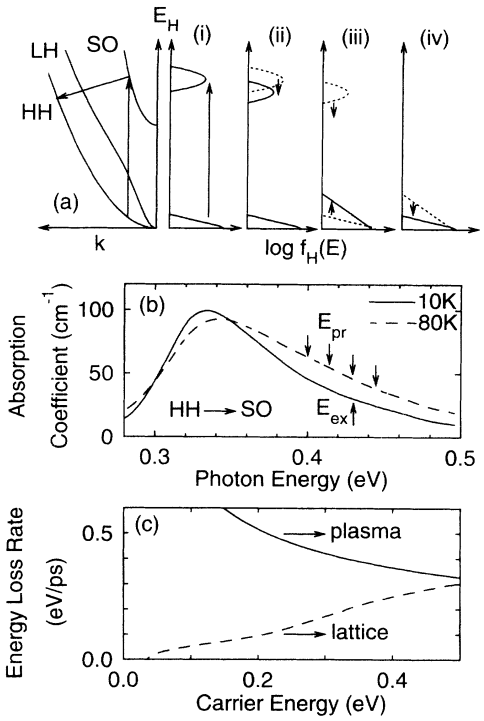

FIG. 1. (a) Left-hand side: schematic of heavy-hole (HH), light-hole (LH), and splitoff (SO) valence bands is germanium. HH to SO excitation by infrared photons and inter-valence-band scattering by emission of optical phonons are indicated by arrows. Right-hand side: hole distribution functions $f_H(E)$ are plotted on a logarithmic scale versus the hole energy E_H for a sequence of processes in the femtosecond experiment: (i) excitation, (ii) inter-valence-band scattering, (iii) thermalization, and (iv) cooling. (b) Stationary HH to SO inter-valence-band absorption of p-type germanium (acceptor concentration 3×10^{17} cm^{-3}) for lattice temperatures T_L of 10 and 80 K. The spectral positions of the femtosecond excitation (E_{ex}) and probe (E_{pr}) pulses are indicated. (c) Calculated energy loss rates as a function of the carrier energy for interaction with a cold hole plasma (solid line) and with the lattice (dashed line).

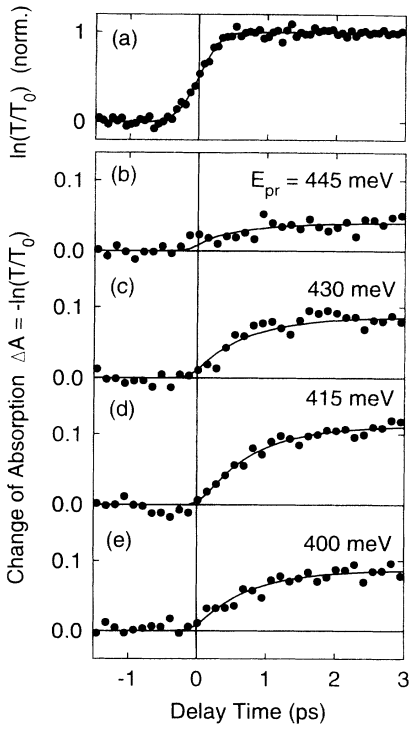

FIG. 2. (a) Time-integrated cross correlation function of the femtosecond mid-infrared pump and probe pulses, determining time zero and the pulse durations of $t_P \simeq 250$ fs. (b)–(e) Transient increase of HH to SO inter-valence-band absorption of p-type germanium after femtosecond excitation at $E_{ex}=430$ meV (2.9 μm and $T_L=10$ K). The change of absorption $\Delta A=-\ln(T/T_0)$ is plotted versus the delay time between pump and probe pulses for four probe energies E_{pr} of (b) 445 meV, (c) 430 meV, (d) 415 meV, and (e) 400 meV. (T_0 and T are the transmission before and after excitation).

A numerical analysis assuming monoexponential kinetics gives a common rise time of $\tau_{rise}=700\pm150$ fs for the different spectral positions (solid lines). It is important to note that a transient decrease of absorption is not detected, i.e., spectral hole burning is absent even around delay zero where pump and probe pulses coincide.

In Fig. 3, we present time-resolved data taken at different lattice temperatures T_L of (a) 10 K, (b) 40 K, and (c) 60 K with identical photon energies $E_{ex}=E_{pr}=390$ meV. On the left-hand side, the change of absorption is plotted for the first 2 ps. The data show an increase of absorption with a rise time of $\tau_{rise}\simeq700$ fs for the different T_L values. The induced absorption decays with a picosecond kinetics depending upon the specific lattice temperature (right-hand side of Fig. 3). For $T_L=10$ K [Fig. 3(a)], we observe a long recovery time of several hundreds of picoseconds whereas a considerably faster relaxation is found at higher lattice tem-

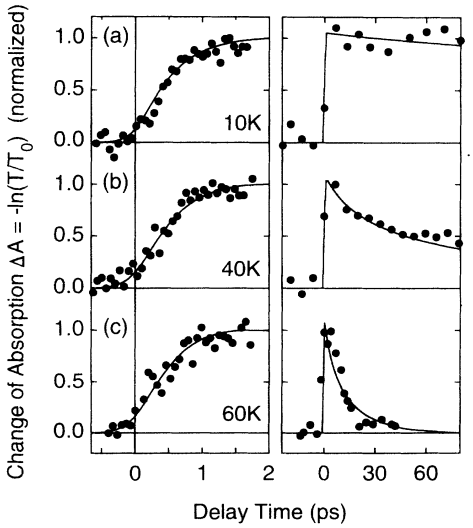

FIG. 3. Time-dependent increase of absorption after excitation and probing at 390 meV for lattice temperatures T_L of (a) 10 K, (b) 40 K, and (c) 60 K. The signal is normalized to its peak value. Left-hand side: femtosecond rise of the signal. Right-hand side: picosecond decay of the transient absorption due to cooling of the hole plasma.

peratures [Figs. 3(b) and 3(c)].

We now discuss the scattering events occurring during and after femtosecond excitation of holes via the HH to SO transition. In Fig. 1(a), the different processes are visualized schematically with the help of the hole distributions (i)–(iv).

(i) Excitation. Absorption of pump photons leads to a transient depletion of HH states and to an excess population of SO levels that are optically coupled by the femtosecond excitation pulse. These changes of the hole distribution are expected to cause a *decrease* of inter-valence-band absorption by state filling on an ultrafast time scale (spectral hole burning). However, this effect is clearly not observed. In fact, our data show an *increase* of absorption for all spectral positions and delay times. This finding demonstrates that within our time resolution of 100 fs the holes excited to the SO band scatter rapidly out of the optically coupled region in **k** space and that the HH states depleted by the pump pulse are quickly repopulated. The latter quasiequilibrium is accomplished by collisions among unexcited holes with small changes in the **k** vectors.[16]

(ii) Inter-valence-band scattering and (iii) thermalization. In our experiments, the total carrier concentration is constant. As a result, population of SO states corresponds to a reduced density of heavy holes and a decrease of absorption at any spectral position in the HH to SO band [cf. Fig. 1(b)]. The holes excited to the SO band undergo two major relaxation processes, inter-valence-band scattering by emission of optical phonons and thermalization. There are two alternative relaxation schemes. In the first model, the thermalization rates are much higher than the rate of inter-valence-band scattering. Here the small number of SO holes undergo a fast intra-SO band equilibration by inelastic scattering with the large number of unexcited HH holes, resulting in an elevated HH temperature. On a slower time scale, the thermalized SO holes are scattered back to the HH band by emission of optical phonons. Subsequently, the backscattered holes thermalize by emission of optical phonons and, mainly, by interaction with unexcited heavy holes, strongly heating the HH distribution and enhancing the population of HH states that are monitored at the different probe frequencies.

In the time-resolved HH to SO absorption, such a relaxation scheme would result in an initial bleaching, followed by a first rapid rise of absorption caused by the SO equilibration and a second delayed increase of absorption due to thermalization of the backscattered heavy holes. The relative strength of the three contributions should change drastically with probe frequency [cf. Fig. 1(b)]. This behavior does not agree with our data, which do not show bleaching and/or an absorption rise at early times but exclusively a delayed monoexponential increase of absorption.

In contrast, our experimental results agree with the relaxation scheme depicted in Fig. 1(a) where inter-valence-band scattering is fast compared to HH thermalization. The holes excited to SO states scatter back to the HH band within the time resolution of our experiments. This initial step is followed by thermalization within the HH band and heating of the cold Fermi sea, giving rise to the observed delayed increase of HH to SO absorption. Thus our data directly show that the heavy-hole thermalization proceeds with a time constant of 700 fs.

The latter interpretation is supported by theoretical calculations. The rates of intervalence band scattering via the optical deformation potential were calculated in first-order perturbation theory taking into account the nonparabolic valence-band structure and the k-dependent overlap of the corresponding hole wave functions.[17,18] A previously determined value of $D_0 = 6.3 \times 10^8$ eV/cm was used for the deformation potential.[14] We estimate a very short lifetime of $\tau_{SO} = 100$ fs for carriers in the SO band. From the same formalism, we calculated the phonon scattering rates within the HH band that are plotted in Fig. 1(c) (dashed line).

Inelastic hole-hole scattering is treated in a model including the full dynamical screening of the Coulomb interaction as well as intra- and inter-valence-band transitions.[19,20] Here a single carrier loses energy by scattering with the fluctuations of the longitudinal macroscopic electric field in the plasma of unexcited holes at wave vectors q and frequencies ω. The longitudinal dielectric response function $\epsilon(q,\omega)$ is calculated in random-phase approximation.[21] The calculated energy loss rate (dE/dt) is plotted as a function of carrier energy in Fig. 1(c) (solid line). For $E_H \simeq 500$ meV, (dE/dt) has roughly the same value as the phonon emission rate (dashed line), whereas carrier-carrier scattering dominates at smaller excess energies. Excitation of HH to light-hole *inter-valence-* band transitions in the cold plasma represents the main mechanism by which hot holes lose their excess energy. The weak *dynamical* screening of the Coulomb interaction among the carriers is essential to account for the observed high scattering rates.[5,16] A time constant for the thermalization process is defined as $\tau_{\text{therm}} = E_H (dE_H/dt)^{-1}_{\text{loss}}$. For holes with $E_H = 400$ meV, we estimate $\tau_{\text{therm}} \simeq 0.5$ ps, which is in good agreement with our experimental results [Figs. 2(b)–2(e) and 3(a)–3(c)].

(iv) Cooling. The transient absorption reaches its maximum $\Delta A_{\max}(E_{\text{pr}})$ at a delay time of $t_D \simeq 3$ ps. Within the experimental accuracy, $\Delta A_{\max}(E_{\text{pr}})$ corresponds to the difference between the stationary absorption spectra for $T_L = 10$ and 80 K [cf. Fig. 1(b)]. Cooling of the hot holes down to lattice temperature T_L represents the final relaxation process.[14] For $T_L = 60$ K [Fig. 3(c)], emission of optical phonons via the deformation potential leads to carrier cooling within 50 ps. For lower (carrier and lattice) temperatures, the fraction of holes emitting optical phonons is reduced and acoustic phonon scattering determines the substantially slower relaxation kinetics [Figs. 3(a) and 3(b)].

In conclusion, the results presented here give a convincing picture of different ultrafast relaxation processes of holes. Femtosecond infrared studies of p-type germanium reveal that equilibration within the bath of cold carriers occurs in the regime below 100 fs and that holes excited to the splitoff band scatter back to high-lying heavy- and light-hole states within 100 fs. We demon-

strate that the subsequent thermalization of the excited carriers proceeds on a time scale of 700 fs, predominantly by inelastic scattering with unexcited holes. The high energy loss rates are due to the weak dynamical screening of the Coulomb interaction in the carrier system. This scheme of hole thermalization is relevant for other semiconductors such as GaAs, which shows similar valence-band parameters, optical deformation potentials, and, consequently, scattering rates of holes.

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