Direct observation of electron relaxation in intrinsic GaAs using femtosecond pump-probe spectroscopy

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The evolution of a nonequilibrium photoinjected electron population is investigated independently of the hole population using femtosecond pump-probe transmission in an unconventional configuration with the absorption saturation measured from the unoccupied spin-orbit-split valence band. Ultrafast electron relaxation is observed: within 40 fs the excited electrons are redistributed down to the band gap even for densities as low as 10^{17} cm^{-3}. Thermalization of the electron distribution is achieved already 200 fs after the end of the pump pulse. The electron temperature can be obtained as a function of time and an absorption increase observed at long times is attributed to a Fermi-edge singularity.

The relaxation of nonequilibrium carrier distributions is of fundamental interest in semiconductor physics and plays a crucial role in the development of high-speed optoelectronic devices. Carrier-carrier, longitudinal-optical (LO) phonon, and intervalley scattering contribute to the relaxation of the carrier distributions with a weight depending on the excitation energy and density. A large variety of femtosecond and picosecond spectroscopic techniques have been employed in order to elucidate the evolution of an initially peaked photoinjected population towards a thermalized hot Fermi distribution and to measure the carrier-carrier scattering times.[1–10]

Pump-probe experiments[1–6] are based on the absorption saturation caused by the carrier distributions, due to the Pauli exclusion principle. Neglecting band-gap renormalization and excitonic effects, the changes in absorption coefficient are proportional to the sum of the electron and hole distribution functions (f_e and f_h, respectively):

$$-\Delta\alpha = \alpha_0 - \alpha = \alpha_0(f_e + f_h), \tag{1}$$

where $\alpha_0(\alpha)$ is the absorption coefficient of the unexcited (excited) sample. Therefore, it is difficult to extract information concerning the electron and hole populations separately. Furthermore, coherence effects can significantly distort the differential absorption signal close to zero pump-probe delay time.[11] While the contribution to the signal of the perturbed free polarization decay term is small for an almost flat density of states, the pump polarization coupling (induced grating) term cannot be neglected if pump and probe are at the same wavelength.[11,12]

Luminescence up-conversion measurements,[8] on the other hand, are proportional to the product $f_e f_h$ of the distribution functions. They, therefore, do not permit the separate monitoring of the electron and hole dynamics and neither do photon-echo experiments.[7]

A possible way to isolate the evolution of the electron population is to use electron-acceptor recombination in p-type material.[9,10] Since this luminescence does not involve the optically excited holes, direct studies of the electrons are feasible. However, the material under study is not the intrinsic semiconductor and the results may be quite different due to electron-impurity scattering.[10]

Here, we present an approach to measure the electron dynamics independently. We have also used the pump-probe scheme with the difference that the probe pulse probes the absorption saturation of the transition from the spin-orbit-split valence band to the conduction band (SO-C). The principle of this technique is shown in Fig. 1. The pump energy is chosen low enough to excite electrons only from the heavy- (HH) and light-hole (LH) valence bands. Thus, no holes are present in the SO band and the differential absorption signal becomes sensitive to f_e only, since f_h equals 0. The additional advantage of this method is that the electron population can be tested at the energy at which it was created, but with a probe pulse of a different wavelength. In this way, coherence effects are avoided and the signal is determined by the population term. Moreover, the electron distribution can be readily observed close to the conduction band edge without interference from a strong exciton-bleaching signal. Indeed, the SO-C exciton peak is much weaker than the exciton peak at the fundamental band gap (see inset of Fig. 1), whose bleaching causes large differential absorption signals in conventional pump-probe experiments.

Pump-probe transmission with a probe testing the SO-C transition has previously been used by Feldmann *et al.*[13] in order to confirm that the measured $\Gamma \rightarrow X$ intervalley scattering rates in type-II GaAs/AlAs superlattices were indeed due to electron and not to hole transfer. Efforts to use this technique to study electron thermalization in GaAs were hampered by the large absorption of the $Ga_{0.7}Al_{0.3}As$ etch-stop layer.[14]

Our sample consists of a 0.65-μm-thick GaAs layer sandwiched between two $Ga_{1-x}Al_xAs$ layers grown by molecular-beam epitaxy on a GaAs substrate. The substrate was selectively etched away and antireflection coatings were deposited on both sides of the sample in order to avoid Fabry-Perot interference fringes. The Al concentration in the $Ga_{1-x}Al_xAs$ layers was expressly chosen to be high ($x \simeq 0.65$) so that their absorption lies much higher than the SO-C transitions of interest here. The

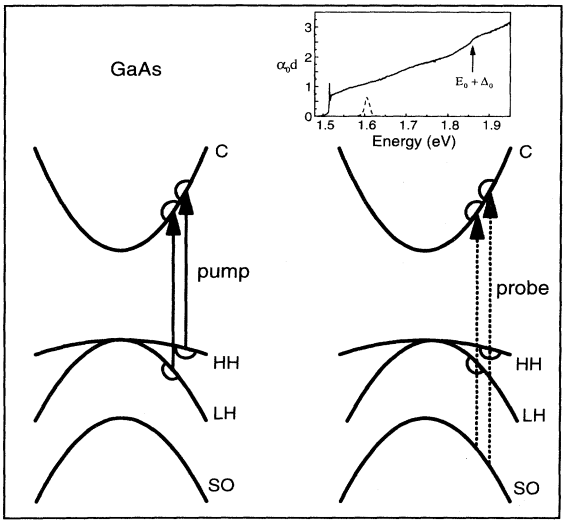

FIG. 1. Schematic band structure of GaAs indicating the transitions undergone under excitation with the pump pulse (solid arrows) and the transitions tested by the probe pulse (dashed arrows). The inset shows the linear sample absorption ($\alpha_0 d$, where d is the sample thickness) and the pump spectrum centered at 1.606 eV (dashed line) in arbitrary units. A shoulder is seen in the linear absorption at the onset of transitions from the split-off valence band (see arrow).

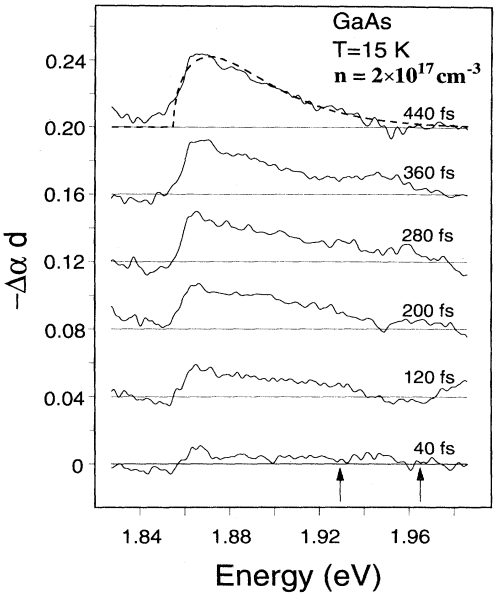

FIG. 2. Differential absorption spectra for several early pump-probe delay times. We fix the zero of delay at the first nonzero differential spectrum that is at the beginning of the pump pulse. Thus the spectrum at a delay of 280 fs corresponds approximately to the end of the pump pulse, which is confirmed by the fact that the area of the differential absorption spectra stops increasing. The two arrows at 1.965 and 1.928 eV indicate the central positions of the nonequilibrium electron distributions excited from the HH and LH valence bands, respectively, as tested from the SO band. (The masses used are $m_e=0.067m_0$, $m_{hh}=0.38m_0$, $m_{lh}=0.082m_0$, $m_{so}=0.15m_0$.) The dashed curve is a Fermi-Dirac function (electron temperature $T_e=170$ K) multiplied by the density of states.

linear absorption of our sample is shown in the inset of Fig. 1.

The pump-probe experiments were performed using a colliding-pulse mode-locked laser operating at 620 nm amplified at 6.5 kHz with the green line of a copper vapor laser (CVL). Two different spectral continua are formed by splitting the amplified beam and by focusing it on two ethylene glycol jets. For the first, the intensity is kept close to the threshold of continuum generation in order to obtain a more stable continuum from 625 to 675 nm for the probe pulse, while pump pulses with energies up to 100 nJ are obtained by selecting part of the second continuum with an interference filter and further amplifying it in a four-pass amplifier[15] also pumped by the green line of the CVL. We compensate the chirp of the pump pulse with a pair of prisms and that of the probe pulse with a combination of prisms and gratings in order to correct up to the third derivative of the phase.[16] We obtain a full width at half maximum duration of 40 fs for the probe and 140 fs for a 15-meV wide pump pulse. The probe and pump are perpendicularly polarized and focused down to 90 and 180 μm spots, respectively, onto the sample which is held at 15 K.

Several differential absorption spectra ($-\Delta\alpha d$) for different pump-probe delay times are shown in Fig. 2. The pump spectrum is shown in the inset of Fig. 1 and the electron density estimated from the pump intensity and from the area of the differential absorption spectrum is 2×10^{17} cm^{-3}. While the electrons excited from the HH and LH valence bands should appear at 1.965 and 1.928 eV, as tested from the SO band, we observe a practically simultaneous rise of the induced transparency at all energies from 1.965 eV down to the SO-C band gap at 1.855 eV. (The induced transparency is slightly more pronounced close to the band gap already at very early delay times, possibly indicating a small contribution of carrier-induced bleaching of the SO-C discrete exciton.) This demonstrates that the initially excited nonequilibrium electron population is redistributed extremely rapidly over the whole energy range down to the band gap within 40 fs, the time resolution of our experiment. We performed measurements at different carrier densities and observed the same ultrafast initial relaxation of electrons for densities ranging from 9×10^{16} cm^{-3} to 4×10^{17} cm^{-3}.[17]

We remind you here that the measured signal is insensitive to the absorption saturation caused by the holes. We, thus, can follow the evolution of the electron population as a function of delay time with a 40-fs resolution given by the duration of the probe pulse. The luminescence experiments of Elsaesser *et al.*[8] evidenced a redistribution of electrons over a wide energy range within their time resolution of 100 fs for a density of 1.7×10^{17} cm^{-3}. Our experiment reduces this upper limit for the electron redistribution time down to 40 fs for similar carrier densities and it additionally permits the direct monitoring of the evolution of the electron population towards a thermalized distribution that can be described by a Fermi-Dirac function.

The influence of excitonic effects in our measurements has to be considered. As mentioned above, the contribution of the discrete exciton is negligible. The Coulomb enhancement factor of the SO-C continuum excitons[18] can be reduced by the presence of the carriers giving rise

to a positive $-\Delta\alpha$ signal. According to Ref. 19, though, there is a significant reduction only for densities much larger than the ones involved here (above 10^{18} cm^{-3}) for thermalized distributions. A recent paper[20] predicts a larger reduction of the Sommerfeld factor for nonequilibrium peaked distributions. This work may, however, not apply to our experiment since it is based on theory valid for thermalized populations and on a statically screened Coulomb potential. In any case, both Refs. 19 and 20 deal with the fundamental band gap and still little is known about the screening of SO-C transitions. In short, while a small contribution due to the reduction of the Coulomb enhancement factor may appear in our signal, it cannot explain the ultrafast rise at all energies from the initial excitation energy down to the SO-C gap, especially given the fact that no hole-burning signal associated with a peaked distribution is observed. The coherent coupling between the pump pulse and the interband polarization[21] cannot account for this rise either.

Quite a few pump-probe transmission experiments in the conventional configuration with pump and probe at the same wavelength[2,3,6] have shown positive differential absorption peaks at the spectral position of the initially injected carriers. These peaks were attributed to dynamical spectral hole burning by carrier populations that have not had enough time to completely relax at the time scale of the observation. We have checked that we also observe a differential absorption peak in the conventional configuration (the rest of the conditions being similar) and we believe that the reason no distinct peaks are discernable in our configuration is that their magnitude is much smaller. As mentioned above, part of the signal in the conventional configuration is due to diffraction of the pump in the direction of the probe (induced-grating term). Assuming equal intensities for the population and for the induced-grating term,[11,14] the expected intensity of the population term is only half of the total signal. In the conventional configuration, the signal is due to the presence of electrons and holes. Supposing no relaxation has taken place, $f_e=f_h$ and the expected signal in our configuration is reduced by a further factor of 2. An additional factor of about 2 is obtained when one considers the absorption coefficients involved and the fact that in the conventional configuration the electron populations excited from the HH and LH bands are tested at the same wavelength, which is not the case when they are probed from the SO band. Only a small reduction of a factor of 1.2 is due to the smaller mass of the SO band compared to that of the HH band, which leads to a broadening of the hole-burning signal. Indeed, the width of the hole-burning signal is mainly determined by the lighter electron mass. However, the shorter lifetime of the hole in the SO band (85 fs at the Γ-point according to Ref. 22) as compared to the lifetime in the HH and LH bands leads to an increased intrinsic width of the signal. In our case, though, this intrinsic width is comparable to the pump spectral width. In total, the expected magnitude of the signal is about ten times smaller than in the conventional configuration and is within the noise of our experiment.

The spectra of Fig. 2 show a very fast electron thermalization. The differential absorption spectrum at 280 fs, approximately at the end of the pump pulse, shows small deviations from a Fermi-Dirac distribution while the curve at 440 fs, only 100–200 fs after the end of the pump, is already nicely fitted by a Fermi-Dirac distribution function (with an electron temperature T_e=170 K) multiplied by a square-root dependence for the density of states. (The fit is not so good on the low-energy side, because no broadening was taken into account.) The temperature of 170 K is already much lower than the temperatures corresponding to the initial excess energies of the electrons excited from the HH and LH bands, 73 and 48 meV, respectively. This cooling during the thermalization process is consistent with the emission of one or two LO phonons per electron and is in agreement with the LO-phonon emission time of about 150 fs. However, electron-phonon scattering is not fast enough to explain the rapid electron thermalization within 200 fs. We thus conclude that carrier-carrier scattering is the dominant thermalization mechanism, for the densities explored here, while intervalley scattering is negligible due to the low initial electron energy compared to the energy of the L and X valleys.

Fits similar to that in Fig. 2 allow the determination of the electron temperature as a function of time (as is shown in Ref. 17), in contrast to luminescence measurements that yield a combination of the electron and hole temperature. The rapid thermalization of the electron system does not imply a thermalization of the electron-hole plasma, i.e., a common temperature for electrons and holes. Indeed, theoretical[23] as well as experimental findings in steady-state conditions[24] show that the temperatures and energy-loss rates of electrons and holes can be significantly different. It is therefore important to compare calculations of energy-loss rates to *electron* and not to combined electron and hole cooling curves in order

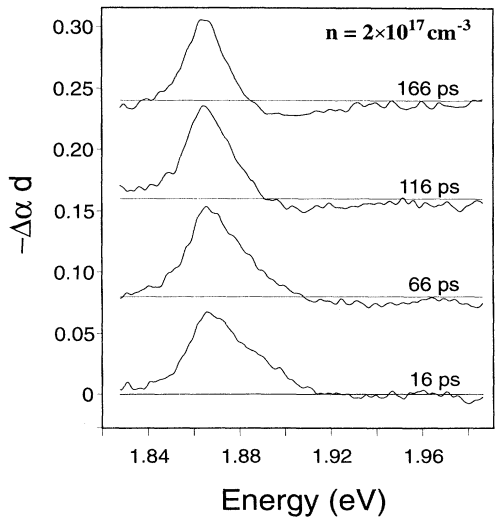

FIG. 3. Differential absorption spectra for long pump-probe delay times. As the electron temperature decreases (from 70 K for the bottom spectrum to 35 K for the top one), a negative signal appears on the high-energy side of the electron distribution attributed to a Fermi-edge singularity. A small population decrease is also visible for the longest delay times.

to draw conclusions about issues like hot-phonon effects, screening, and the role of reduced dimensionality.

For electron temperatures below 70 K, a negative differential absorption signal corresponding to an absorption increase appears on the high-energy side of the electron distribution and increases as the electron temperature drops (see Fig. 3). This temperature dependence is characteristic of the so-called Fermi-edge singularity,[25] the enhancement of the absorption near the Fermi level as a result of the dynamical rearrangement of the electron Fermi sea in the presence of the heavier hole created by the probe pulse in the SO valence band. This many-body effect has been principally studied in modulation-doped quantum wells[26] and its observation necessitates a sharp Fermi edge. Foing *et al.*[6] reported its appearance in intrinsic GaAs on the high-energy side of a nonequilibrium Fermi sea created by the pump pulse. In the latter case, the increased absorption disappears immediately after the end of the pump pulse, because carrier-carrier scattering smears out the peaked distribution. The present observation of a thermalized Fermi-edge singularity in undoped GaAs and its evolution as a function of temperature provides a different material for a comparison between theory and experiment. It is interesting to note that this singularity is observed despite the relatively light SO mass (only two times heavier than that of the electron).

In conclusion, femtosecond pump-probe spectroscopy using the unoccupied split-off valence band to measure the electron-induced absorption saturation permits the direct observation of an initially nonequilibrium electron population and its evolution towards equilibrium within the electron system and then with the lattice. Our measurements set an upper limit of 40 fs for the redistribution of 10^{17} cm^{-3} electrons and show a thermalized distribution within 200 fs after the end of the pump pulse.

The separate monitoring of the electron population opens up possibilities for comparison with carrier-relaxation and energy-loss rate calculations. Indeed, results obtained from the joint observation of electrons and holes can and should be revisited. One of the limitations of our technique is that small absorption saturation signals of the SO-C transition have to be detected on top of a constant absorption background, due to HH-C and LH-C transitions at the same energies. We are working on the improvement of the signal-to-noise ratio, which should permit an extension of this technique to electron densities down to 10^{16} cm^{-3} or below.

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