RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 20 15 NOVEMBER 1994-II

Rapid Communications

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Parabolic valence-band dispersion in GaAs for optical interband transitions

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(Received 7 June 1994; revised manuscript received 22 August 1994)

The initial nonthermal electron distribution at densities $\leq 10^{14}$ cm^{-3} is studied in GaAs:Be by investigating the band-to-acceptor luminescence after excitation by picosecond laser pulses. Two peaks are observed originating from electrons generated out of the heavy- and light-hole valence bands, respectively. This assignment is confirmed by polarization dependence. Variation of excitation energy yields the valence-band dispersions for wave vectors $<0.04(\pi/a)$, where purely parabolic terms dominate. The light- and heavy-hole masses relevant for optical interband excitation of a 100 GaAs surface close to the band edge are determined to be $m_{\rm lh}=0.093m_0\pm 0.007m_0$ and $m_{\rm hh}=0.54m_0\pm 0.05m_0$.

An accurate knowledge of the band structure in the vicinity of the gap is useful for many optical and transport experiments. The conduction-band dispersion and the electron mass of GaAs are known very well and with high accuracy.[1] However, the exact values for the light- and heavy-hole masses and the valence-band dispersions were still discussed until very recently.[2–7] In particular, it is not obvious which effective hole mass should be used for optical interband transitions. The reason for the discrepancies is the complicated valence-band structure: anisotropy and nonparabolicity require appreciable corrections already for small hole energies and momentum vectors. In detail, the following effects must be included in the different experimental methods: cyclotron experiments[8] require inclusion of nonparabolicity and polaron corrections, the experiment is done at elevated temperatures, and only an average mass in the plane perpendicular to the magnetic field is measured. Consequently, the cyclotron masses differ from the band effective masses.[4] In magneto-optical experiments[5,9,10] excitonic effects and spin splittings complicate the interpretation of the data, in particular, since the magnitude of these effects depends on the magnetic field strength. Spectroscopy on GaAs/Al$_x$Ga$_{1-x}$As quantum wells[2,3] is also not easy to interpret since excitonic effects and band-gap renormalization are particularly pronounced in these heterostructures. Theoretical analysis of acceptor spectra[4] should be accurate but is nevertheless a rather indirect method to determine the valence-band dispersion. Most recently, hot electron-to-acceptor recombination in cw photoluminescence experiments was used to extract the valence-band dispersion.[6,7,11,12] This method rather directly visualizes the valence-band dispersion relevant for optical interband excitation; however, these experiments revealed only a regime in k space where nonparabolicity already appreciably contributes to the dispersion.

We present here similar photoluminescence experiments, but time-resolved with a time resolution of 10 ps and with pulsed excitation. The valence-band dispersion not only of the heavy but also from the light hole is in our experiment directly visualized. Reliable values for the effective masses directly at the band edge are obtained, i.e., for small k values where the dispersions are still completely parabolic. Our experiments yield values for the heavy- and light-hole masses which are relevant for optical interband excitations of a 100 GaAs surface close to the band edge. These are the appropriate values when, e.g., the thermalization processes after short pulse excitation are studied in time-resolved experiments and analyzed in model calculations.[13–21]

At medium to high densities electrons form a thermal, Maxwell-Boltzman distribution within a few hundred femtoseconds after excitation.[19] But at very low densities carrier-carrier scattering is strongly reduced and thermalization times up to 50 ps occur.[20] Recently, a clear nonthermal electron distribution on a picosecond time scale was found in the band-to-acceptor transition in GaAs:Ge after excitation by a short laser pulse at densities $\leq 10^{14}$ cm^{-3}.[20] However, the initial nonthermal electron distribution at $t=0$ was always broader in energy than expected theoretically. Spatial electron-hole correlation immediately after excitation was first suggested as a possible explanation for the fast initial broadening.[20] Later, an explosive broadening of the initial electron distribution was calculated.[22] However, both effects could not be reproduced by molecular dynamics[23] or Monte Carlo simulations.[24] Germanium was used in the first experiments[20] as an acceptor because of the large acceptor binding energy of 40.4 meV, which helps to separate the band-to-acceptor transition from the band-gap luminescence and which prohibits acceptor ionization as possible energy-loss mechanism for the electrons. But Ge is an amphoteric dopant and acts both as an acceptor and as a donor in a ratio of approximately 3:1.[25] In thermal equilibrium, all donors

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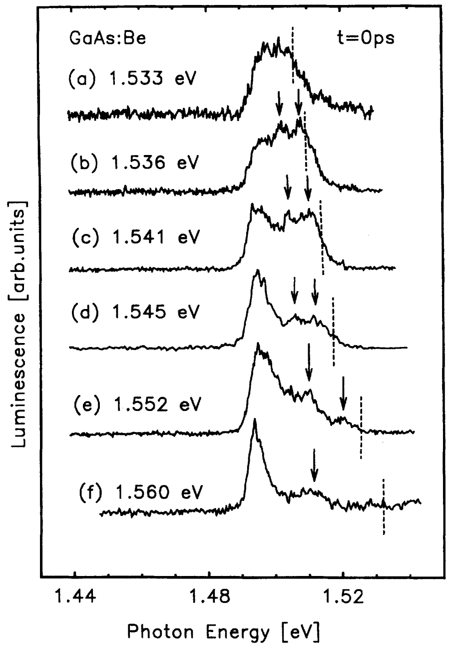

FIG. 1. Initial band-to-acceptor luminescence in GaAs:Be for excitation density of 10^{14} cm^{-3}. The laser photon energies are (a) 1.533 eV, (b) 1.536 eV, (c) 1.541 eV, (d) 1.545 eV, (e) 1.552 eV, and (f) 1.560 eV. Vertical dashed lines: energies corresponding to the laser photon energy minus 28 meV for the acceptor binding energy. Two nonthermal electron distributions are observed for laser photon energies > 1.534 eV. The arrows are at the peak positions of the corresponding band-to-acceptor transitions.

should be ionized and therefore should not contribute to the thermalization. However, in the time-resolved experiment, a quasistationary neutral donor concentration is present due to the high repetition rate of the pulsed laser compared to the slow rate of donor-acceptor pair recombination. This pair recombination actually shows up as a long-lived luminescence at the low-energy side of the band-to-acceptor transition and has to be subtracted in order to make an analysis of the transient band-to-acceptor recombination possible.[20] Recent Monte Carlo simulations[24] indicated that the contribution from ionization of these neutral Ge donors to the thermalization process might be stronger than estimated up to now. Thus, a contribution of ionization of donors to the initial broadening cannot be excluded.

In our experiments, we use beryllium, an exclusive acceptor, in order to eliminate donor ionization as thermalization process. Indeed, the initial nonthermal electron distribution in GaAs:Be in our experiment shows two peaks, which are caused by excitation from the heavy-hole (hh) and light-hole (lh) valence bands, respectively. This is the first time, to the best of our knowledge, that in time-resolved experiments the two electron distributions originating from the two valence bands are seen. The direct experimental determination of the valence-band dispersions $E_{\mathrm{hh}}(k)$ and $E_{\mathrm{lh}}(k)$ for very small wave numbers becomes possible.

The sample used in our experiment is GaAs:Be grown by molecular beam epitaxy. The room-temperature hole concentration is 6×10^{16} cm^{-3}. The sample is kept at a temperature of about 10 K on the cold finger of a He cryostat. Carriers are generated near the Γ-band minimum using a ps titanium:sapphire laser with a pulse width (full width at half-maximum) of 1–2 ps and a repetition rate of 80 MHz. The luminescence is spectrally dispersed in a 0.3-m monochromator and time-resolved detected using a synchroscan streak camera. Temporal and spectral resolutions are 10 ps and 1 meV, respectively.

Two nonthermal electron distributions are produced by exciting electrons from the light-hole and heavy-hole valence bands into the conduction band with an excitation photon energy 7–36 meV above the band-gap energy. The excitation density is $\leqslant 1\times10^{14}$ cm^{-3}. The nonthermal electron distributions evolve into a thermal electron distribution within about 50 ps, mainly by electron-electron scattering. The band-to-acceptor luminescence during excitation by the laser pulse directly yields the initial nonthermal electron distribution. Figure 1 shows the initial spectra of the band-to-acceptor recombination in GaAs:Be for various laser photon energies at excitation densities of about 1×10^{14} cm^{-3}. The vertical dashed lines are at the energies which correspond to the photon energy of the exciting laser minus 28 meV acceptor binding energy of beryllium. The band-to-acceptor luminescence for the lowest excitation energy (curve a) consists of one single, unresolved, broad, nonthermal electron distribution. For excitation energies above 1.534 eV, however, the luminescence spectra split into three peaks (curves b–f). The positions of the two peaks at higher energies are indicated in Fig. 1 by arrows and fit quite well the theoretically expected positions of the initial nonthermal electron distributions generated for a given excitation energy from the light-hole and heavy-hole valence bands, respectively. Their energy increases with increasing excitation energy. For the highest excitation energy (curve f) the energy of electrons generated from the heavy-hole band exactly matches the LO-phonon energy. In this case, scattering with LO phonons removes the high energetic electrons within our time resolution and forms a cold distribution at the bottom of the band.

Surprisingly, a similar low-energy peak can be seen also for electron excess energies $<\hbar\omega_{\mathrm{LO}}$ (curves b–e). The origin of this peak, not observed in GaAs:Ge, has not been clarified up to now. Very fast ionization of beryllium acceptors could be a possible mechanism to explain this evolution of low-energy electrons, as the electron excess energy is close to the acceptor ionization energy of 28 meV. Monte Carlo simulations including acceptor ionization[24] indeed confirm a dramatic increase of the thermalization rate with increasing laser photon energy, but are unable to reproduce the fast appearance and, in particular, the Maxwell-Boltzmann-like shape of this peak.

Up to now, the polarization of the excitation was linear. Both conduction-band spin states $CB_{+1/2}$ and $CB_{-1/2}$ are then occupied equally.[26] The transition rules are different when using circular polarization for excitation. Four transitions are possible in this case:[26]

$$\mathrm{hh}_{+3/2}\rightarrow CB_{+1/2} \quad \text{for } \sigma^{-}, \tag{1a}$$

$$\mathrm{lh}_{+1/2}\rightarrow CB_{-1/2} \quad \text{for } \sigma^{-}, \tag{1b}$$

$$\mathrm{lh}_{-1/2}\rightarrow CB_{+1/2} \quad \text{for } \sigma^{+}, \tag{1c}$$

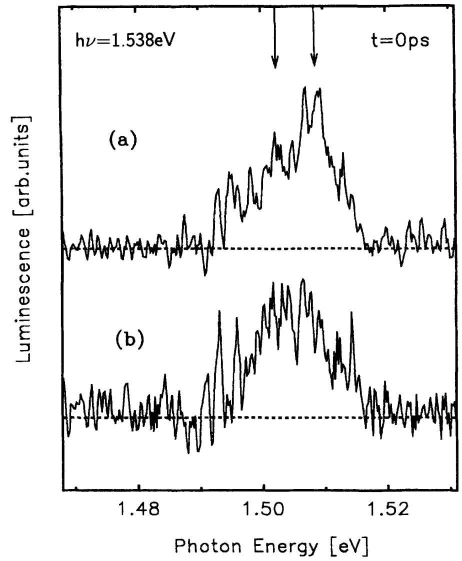

FIG. 2. Band-to-acceptor luminescence spectra for GaAs:Be during excitation by a 2-ps laser pulse at 1.538 eV for two polarization conditions: (a) excitation circularly polarized, luminescence observed through an analyzer of same handedness; (b) excitation circularly polarized, luminescence observed through an analyzer of opposite handedness. Arrows: calculated initial peak positions for electrons excited from the heavy- and light-hole valence bands, respectively.

$$\mathrm{hh}_{-3/2} \rightarrow CB_{-1/2} \quad \text{for } \sigma^+. \tag{1d}$$

The symbols σ^+ and σ^- refer to the right-hand and left-hand rotating dipoles, respectively, and $\mathrm{hh}_{3/2}$ labels a heavy-hole band with $m_j = 3/2$. Electrons generated from the heavy-hole and light-hole valence bands by circularly polarized light initially differ in their spin orientations. The acceptor wave function, on the other hand, is mainly composed by heavy-hole-like contributions.[26] We can therefore selectively study the nonthermal electron distributions of electrons from the heavy-hole and light-hole valence bands by using a circular polarizer for analyzing the band-to-acceptor luminescence. The result is shown in Fig. 2. The carriers are excited with a laser pulse of 1.538 eV, which has passed through a circular polarizer. The luminescence during excitation is detected using an analyzer of either same handedness (upper curve) or opposite handedness (lower curve) compared to the reflected laser light. The calculated excess energy for electrons generated from the heavy-hole and light-hole valence bands are indicated in Fig. 2 for comparison by arrows.

In the case of same polarization of excitation and detection (upper curve), the band-to-acceptor luminescence signal occurs mainly at the high-energy peak, i.e., involving electrons, generated from the heavy-hole valence band. In the case of opposite polarization (lower curve) the contribution of electrons generated from the light-hole band strongly increases.

The polarization is incomplete due to the following reasons: first, the wave function of the acceptors also has some light-hole character[26] and, second, the transition rules of Eq. (1) only hold exactly for $k = 0$. Additionally, carrier-carrier interaction between electrons generated from opposite valence bands might rapidly destroy the polarization.

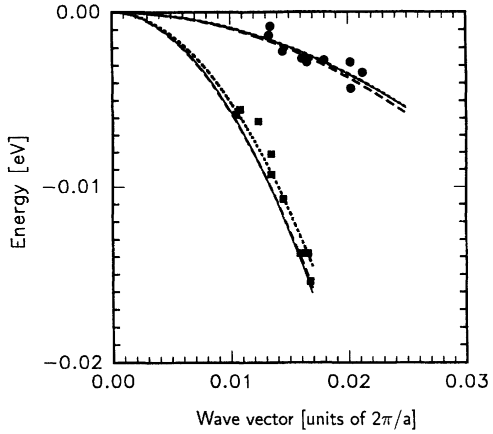

FIG. 3. Heavy- and light-hole valence-band dispersions for very small wave vectors near $k = 0$. Circles and squares: experimental data as calculated from the energetic peak positions of the initial nonthermal electron distributions with an electron effective mass of $0.067m_0$. Dotted line: parabolic fit to the experimental data. Dashed line: nonparabolic effective mass approximation according to Blakemore (Ref. 27). Solid line: zero-order parabolic Luttinger effective mass approximation with $\gamma_1 = 6.85$ and $\bar{\gamma} = 2.5$ (Ref. 30).

The nonthermal electron distribution, observed in our experiment, provides a tool for probing the valence-band dispersions $E_{\mathrm{lh}}(k)$ and $E_{\mathrm{hh}}(k)$ close to the Γ-band minimum for $k < 0.04(\pi/a)$, i.e., a k range, where purely parabolic terms dominate: Carriers are excited by a linearly polarized light with an excitation density of 6×10^{13} cm^{-3}, the photon energy is varied from 1.533 eV to 1.560 eV. The polarization direction is chosen along the [110] direction. The peak positions of the initial nonthermal electron distributions in the band-to-acceptor luminescence directly give the excess energies of the electrons. The corresponding wave vector and the initial hole excess energies can then be calculated[11] using the well known electron effective mass of $0.067m_0$. Figure 3 shows the result. The circles and squares are the measured valence-band energies of the heavy- and light-hole valence bands. The valence-band dispersion using the nonparabolic, isotropic approximation according to Blakemore,[27] with the effective hole masses of $m_{\mathrm{lh}} = 0.082m_0$, $m_{\mathrm{hh}} = 0.51m_0$ and the electron and light-hole nonparabolicity parameter $\alpha = -0.824$ and $\beta = -3.80$ is shown as a dashed line in Fig. 3 for comparison as well as a parabolic approximation with the Luttinger parameters $\gamma_1 = 6.85$ and $\bar{\gamma} = (\gamma_2 + \gamma_3)/2 = 2.50$ (Ref. 30) as a solid line. Quantitative estimations of the contribution of nonparabolicities to the corresponding band dispersion for $k = 0.015(2\pi/a)$ yield 0.9% for the heavy-hole valence-band nonparabolicities and 3.2% for the light-hole valence-band nonparabolicities.[27] Nonparabolic contributions can thus be neglected. Energy terms linear in k, on the other hand, which are nonzero in zinc-blende semiconductors due to the lack of inversion symmetry,[28,29] are too small to significantly contribute to the valence-band dispersion in this k range.[30]

Our experiment is not sensitive to the anisotropy of the valence band. The peak position of the nonthermal electron distribution does not shift if we change the linear polarization from parallel to the [110] axis to parallel to the [100] axis. Only a directional average is detected, which is independent on the polarization direction of the exciting laser light.[7] The energetic peak position which we determine should be close to the position for the [110] dispersion as it was recently proved by line-shape analysis for hot band-to-acceptor luminescence.[7]

A parabolic fit to our experimental data (dotted line in Fig. 3) yields the effective masses $m_{\mathrm{lh}}=0.093m_0\pm0.007m_0$ and $m_{\mathrm{hh}}=0.54m_0\pm0.05m_0$. The precision of the measurement is only limited by the uncertainty in the determination of the peak position as a consequence of the poor signal-to-noise ratio at the low densities necessary for our experiment. However, averaging over the data points reduces the uncertainty. The heavy-hole effective mass is in good agreement with the commonly used values for m_{hh} parallel to the [110] axis. The light-hole effective mass obtained from our experiment is about 5–10 % larger than the values reported elsewhere.[3–5,27,30] However, the experimental uncertainty of our measurement is larger than this deviation.

In conclusion, we have studied the initial nonthermal energy distribution of electrons in GaAs:Be shortly after excitation by a laser pulse. We have seen the energetic splitting between electrons excited from the light- and heavy-hole valence bands. This observation allowed us to experimentally determine the heavy- and light-hole valence-band dispersions $E_{\mathrm{hh}}(k)$ and $E_{\mathrm{lh}}(k)$ for wave vectors $k<0.04(\pi/a)$, i.e., a k range, where purely parabolic terms determine the valence-band dispersion. The results are in reasonable agreement with the commonly used effective hole masses along the [110] crystal direction. For all optical experiments on 100 GaAs surfaces with interband excitation slightly above the fundamental band gap, our effective hole-mass values are the most appropriate since they are directly determined in an optical experiment.

We would like to thank K. Köhler for providing the sample used in our measurements. We would also like to thank P. Supancic and P. Kocevar for helpful discussions and model calculations, as well as D. W. Snoke for helpful conversations. The financial support of the Bundesministerium für Forschung und Technologie and the DAAD is gratefully acknowledged.

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