Band-structure determination of GaAs from hot-electron luminescence

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We show that band-structure information with an accuracy of up to ± 1.0 meV for the first tenth of the Brillouin zone can be obtained from hot luminescence emitted by the transient distribution of laser-excited electrons. With this technique, directionally averaged valence bands can be constructed provided the conduction band is accurately known. It does not allow construction of both the valence band and the conduction band without further information. This new technique is similar to non-angular-resolved photoemission, but its resolution is more than an order of magnitude higher. We demonstrate our new technique for 2×10^{15} -cm⁻³ p-doped GaAs:Ge. Our interpretation is supported by line-shape calculations. Compared with a recent $\mathbf{k} \cdot \mathbf{p}$ calculation, our result puts the light-hole band about 15 meV lower in energy and the heavy-hole band about 7 meV lower. We also obtain information on electronic impurity states associated with higher conduction-band minima. Intra- and intervalley scattering times can be deduced from measuring the intensities of the hot-luminescence spectra.

In the present paper we introduce a method to obtain band-structure information for semiconductors from hot luminescence with a resolution of up to ± 1.0 meV. The method allows the construction of directionally averaged valence bands provided the conduction band is accurately known. Hence band-structure calculations can be tested and other information such as scattering rates and impurity levels at higher conduction-band minima can be obtained.

For many applications such as hot-electron transport there is a need to know the band structure in a substantial part of the Brillouin zone. Most techniques determine band properties only around k=0. Thus $\mathbf{k} \cdot \mathbf{p}$ calculations are based on experimental values of effective masses, gaps, and g values at k=0. High-energy photoemission measures the dispersion in the whole Brillouin zone with low resolution. Drouhin, Hermann, and Lampel^{1,2} recently made an important advance by measuring the energy distribution curves (EDC's) of photoelectrons from 10^{19} -cm⁻³ p-doped GaAs with an energy resolution of about 20 meV.¹

With the method introduced in the present paper we obtain the same kind of information with a precision of up to ± 1.0 meV. This represents an improvement in precision by more than an order of magnitude. An additional advantage of our technique is that samples have low ($\sim 10^{15}$ cm⁻³) doping concentrations. Band-gap shrinkage is negligible for our samples, while it is 30-60 meV for 10^{19} -cm⁻³ p-doped GaAs.^{3,4}

At low temperatures and low carrier concentrations in a polar semiconductor like GaAs electrons high in the conduction band thermalize almost exclusively by LO phonon emission. Therefore, when excited by a single laser frequency the transient distribution of electrons consists of superimposed series of peaks, spaced by about the LO phonon energy: A series for electrons excited from the light-hole band, for the heavy-hole band, and also from the splitoff-hole band (the latter only for sufficiently high laser energies). In the present work we deduce band-structure information from the dependence of the first peak of each series on the dye-laser energy. In addition, we find evidence of a donor level associated with a higher conductionband valley. Luminescence from the transient distribution of hot electrons was first reported by Zakharchenya, Mirlin, and coworkers.⁵⁻⁷ In a recent paper we have shown that the luminescence transition is between hot electrons and holes in acceptor states.⁸ Some concepts are reviewed in Ref. 9.

We have studied a considerable number of Ge-, Zn-, Be-, and C-doped *p*-type GaAs layers grown both by molecularbeam and liquid-phase epitaxy (MBE and LPE) on [100] GaAs substrates. The band-structure study presented here was carried out on a Ge-doped LPE sample with a hole concentration $p = 2.10^{15}$ cm⁻³ as determined by Hall-effect measurements at 77 K. For the present low doping concentrations the acceptor levels do not form an impurity band and there is no band-gap shrinkage^{3,4} due to the doping, as opposed to photoemission experiments.^{1,2} Electron relaxation by intervalence-band scattering¹⁰ will also be absent at our low doping levels.

We used Ar^+ - and Kr^+ -laser-pumped dye lasers, a Jarrel-Ash 1-m double monochromator, a GaAs RCA C31034 photomultiplier, and photon counting apparatus. The sample was in a flowing-He cryostat at 10 K for all measurements reported here.

Figure 1 presents a selection of hot-luminescence spectra for a series of dye laser energies between 1.63 and 2.41 eV. The spectra shown are not corrected for the spectral response of the detection system. The spectra reflect the transient distribution of the hot electrons. The positions of the peaks and Stokes shift change with laser energy. This change contains information on the band structure of the material.

In Fig. 2 we plot the measured peak energies of the first luminescence bands of each of the heavy-hole, light-hole, and split-off series, augmented by the Ge acceptor binding energy,¹¹ as a function of the corresponding laser energy. The sum of the measured peak energies plus the acceptor binding energy is equivalent to the separation of the conduction band from the top of the Γ_8 valence band. The dotted, solid, and dashed lines show the results of a calculation using Rössler's $\mathbf{k} \cdot \mathbf{p}$ matrix¹² in the X, K, and L directions, respectively. For every laser energy the lines for the X, K, and L directions define a range of luminescence energies.

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FIG. 1. Hot luminescence spectra in GaAs:Ge due to transition from the transient distribution of hot electrons to neutral acceptors. The positions of the spectral features as a function of laser energy contain information on the band structure. The asterisk marks a spectral line attributed to a donor associated with a higher conduction-band valley. The spectrum for the highest laser energies shows effects of scattering to other conduction-band valleys.

Calculations presented in Fig. 3 show that the expected luminescence peaks should be near the top of this range. In particular, for the light-hole band the measured peaks lie at the low end of the range. Figure 2 presents our data in a way equivalent to Fig. 9 of Drouhin *et al.*¹ Their photoemission data are shown as full circles, as long as they lie in the energy range considered here.

We would like to stress that the band-structure information we obtain is indirect and averaged over all angles of the wave vector. Thus the experimental points in Fig. 2 are not angularly resolved. In a later section we will show that it is possible to check band-structure calculations by comparing the measured luminescence spectra with the calculated spectra.

The inset of Fig. 2 shows the measured quantities in relationship to the band structure of GaAs, calculated according to Ref. 12. In the inset the relevant transitions are shown as vertical arrows. The inset also shows that angularly averaged experimental points for the valence bands can be constructed assuming that the conduction band is accurately known. By subtracting the value of the band gap and the acceptor binding energy from the energy of the first peak of each series, the value of k' at which the excitation occurred in k space is determined. In construcing this k' value there will be an uncertainty due to the spread of the luminescence peak, a spatial dependence due to the conduction-band anisotropy, and a contribution from the error in the acceptor binding energy. The total uncertainty $\Delta k'$ due to all these effects depends on k'. It is estimated to be less than 4% in



FIG. 2. Peak energies (augmented by the Ge acceptor binding energy $E_{acc} = 40.4 \text{ meV}$) of the first luminescence bands of each series as a function of laser energy (solid squares). The dotted, solid, and dashed lines show the $\mathbf{k} \cdot \mathbf{p}$ calculation (Ref. 12) of the same quantities for the [100], [110], and [111] directions, respectively. Also shown (solid circles) are parts of the results of a photoemission experiment from Ref. 1. The inset shows the relevant transitions in a band-structure diagram of GaAs. The inset also demonstrates that values $\langle E \rangle$ averaged over all angles for the valence bands can be constructed from the present results if it is assumed that the conduction band is known.





FIG. 3. Hot luminescence spectrum in GaAs for laser energy 1.916 eV (solid line). The dotted line shows calculated spectra using the $\mathbf{k} \cdot \mathbf{p}$ matrix from Ref. 12 and the double- δ -function integral (Ref. 13) and appropriate optical transition matrix elements (Ref. 6). The dashed line shows the spectrum from electrons originating from the light-hole (LH) band, determined by subtracting the estimated contribution from the heavy-hole (HH) process. Comparing measured spectra with calculated shapes, the information contained in the shape of the spectra can be interpreted. Note that measured spectra lie significantly below spectra calculated from the $\mathbf{k} \cdot \mathbf{p}$ approximation (Ref. 12).

the present range. $\Delta k'$ is shown as the horizontal error bars in the inset of Fig. 2.

The error $\Delta k'$ for the wave vector of the excitation process at k' is

$$\frac{\Delta k'}{k'} = \frac{\Delta E_c}{2E_c}$$

assuming parabolic bands, where ΔE_c is the error of the acceptor binding energy or the spread of conduction-band energies due to anisotropy. The value for the Ge acceptor binding energy in GaAs is taken from Ref. 11 as $E_{\rm acc,Ge} = 40.4 \pm 1$ meV. The associated error in k' is $\Delta k'/k' < 0.2\%$ in the present range. The wave vector at k' at which the excitation occurred can therefore be fairly accurately determined. Subtracting the value of the laser energy from the conduction-band energy at k', we construct an experimental point for the angularly averaged valence band. The results are displayed in the inset of Fig. 2. Also shown for comparison is the band structure which we calculated using Rössler's $\mathbf{k} \cdot \mathbf{p}$ matrix.¹² We used his calculation for the conduction band in the construction of the experimental points discussed above.

So far it may seem that our experiment only very accurately determines an angular average of the valence bands, provided the conduction band is known. But, in addition to the position of the luminescence peaks, we can also use the information contained in their shape. Using the shape of the spectra allows the accuracy of band structure calculations to be tested far more accurately than using the peak positions alone. To do this, we calculated the shape of the luminescence spectra using the $\mathbf{k} \cdot \mathbf{p}$ parameters of Ref. 12, to use the full sensitivity of our technique. The calculation was done using Allen's double δ -function k-space integra-

tion technique¹³ and the appropriate optical transition matrix elements.⁶ In the present version of the calculation we only include the effect of the anisotropy of the band structure. We do not include lifetime broadening. The result of lineshape calculations for the laser energy $E_L = 1.916 \text{ eV}$ is shown as the dotted line in Fig. 3. Line-shape calculations were carried out for most of our spectra, which in this case were corrected for the spectral response of the detection system. Comparison shows that the measured light valence band lies 15 meV below the $\mathbf{k} \cdot \mathbf{p}$ position in the k region studied here, while the heavy-hole band lies 7 meV below, if the conduction band is accurately determined by the $\mathbf{k} \cdot \mathbf{p}$ calculation.

Inclusion of lifetime broadening in the calculation would be expected to decrease the observed discrepancy in shape and energy position. Note that the spin-orbit splitting of the bands, as a consequence of the absence of inversion symmetry in GaAs, appears as splittings in the calculated luminescence spectra (dotted lines in Fig. 3). The splitting could not be detected in the measured spectra.

The accuracy of the positions of the luminescence peaks (and the shift between different spectra) is around ± 1.0 meV. To exploit this very high precision, which is more than an order of magnitude higher than comparable photoemission experiments, the above-mentioned line-shape calculations are necessary. The difference between calculated and experimental widths can be used to estimate the lifetime of the electrons due to LO phonon scattering and yields a lifetime of around 100 fs.

The spectra in Fig. 1 for dye laser energies between 1.95 and 1.99 eV for Ge-doped GaAs show a peak at 1.739 eV. This peak is marked with an asterisk in Fig. 1. It is absent in C-, Be-, and Zn-doped GaAs. It does not shift with laser energy. The transition must therefore take place between two discrete levels. Our interpretation is, therefore, that it is due to a transition from a donor state related with the Lor the X conduction-band mininum to the neutral Ge acceptor state at Γ . We believe that these donor states are due to Ge atoms on Ga sites. In the case of the donor being at X, using $E(\Gamma_8 - X_6) = 2.010 \pm 0.008 \text{ eV}$,¹⁴ the binding energy would be $E_X^* = 231 \pm 10 \text{ meV} + \langle E_C \rangle$. $\langle E_C \rangle$ is the difference between the peak of the donor-acceptor-pair luminescence band and $E_g - E_A - E_d$ due to the Coulomb interac-tion. $\langle E_C \rangle$ is of the order of 30 meV.¹⁵ E_x^* therefore is close to 260 meV, which is comparable to the binding energy of Ge at X in GaP, 16,17 which is 201.5 meV. In the case of the donor being at L, the binding energy would be $E_L^* = 58 \pm 5 \text{ meV} + \langle E_C \rangle$, using $E(\Gamma_6 - L_6) = 320 \pm 4 \text{ meV}^{18}$. Pressure experiments are necessary to differentiate unambiguously between the two possibilities.

For the future, it is expected that intra- and intervalley scattering times can be deduced from measuring the intensities of the hot luminescence spectra.

In conclusion, we have demonstrated that hot luminescence spectra from the transient distribution of thermalizing electrons contain band-structure information. This information can be extracted from a series of spectra with different dye laser energies. Assuming the conduction band to be accurately known, valence bands averaged over all angles of kare constructed for GaAs in the first tenth of the Brillouin zone. Results of band-structure calculations can be tested in the first tenth of the Brillouin zone with an accuracy up to ± 1 meV using line-shape calculations. The accuracy is more than an order of magnitude higher than comparable photoemission experiments. The present technique uses samples with low doping densities $(10^{15} \text{ cm}^{-3})$, avoiding band-gap shrinkage, which becomes important for concentrations in the 10^{18} cm^{-3} range and above. Although present experiments were done for GaAs, the technique should also be applicable to other materials.

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