High-precision determination of the temperature-dependent band-gap shrinkage due to the electron-phonon interaction in GaAs

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We use temperature-dependent, spatially resolved photoluminescence on a μm scale (μ-PL) to perform high-precision measurements of the band-gap shift in three type-II GaAs/AlAs heterostructures that exhibit narrow luminescence lines from local type-I states. The accuracy of the energy measurements is better than 5 μeV, which allows us to distinguish between the two contributions to the temperature shift, namely lattice expansion and electron-phonon interaction. We explicitly determine the contribution due to electron-phonon interaction at low temperatures. We find that the approach to the electron-phonon spectral function from Collins *et al.* [Phys. Rev. Lett. **65**, 891 (1990)] leads to an excellent fitting function for the high-precision data. From the fit to our data, we determine that the electron-phonon interaction contributes to the asymptotic band-gap shift at high temperatures with $\lim_{T\to\infty}(dE_g/dT)=(-198^{+5}_{-8})\ \mu\mathrm{eV\,K}^{-1}$.

I. INTRODUCTION

The investigation of the temperature dependence of the fundamental band gap in semiconductors is of considerable technological and fundamental interest. The band gap changes with temperature because of two contributions. First, the thermal expansion of the lattice causes a change in the atomic wave-function overlap. Typically, a decrease of the lattice constant causes an increase of the band gap and vice versa. For this contribution, there exists a simple theoretical expression.[1,2] The second contribution is caused by the electron-phonon interaction. There have been various theoretical attempts to calculate this part of the band-gap temperature dependence (see, e.g., Refs. 1–6 and references cited therein). At high temperatures, both contributions lead to a linear change of the band-gap energy. An experimental distinction between the two contributions therefore requires a thorough measurement of the band-gap shift at low temperatures where the electron-phonon interaction clearly dominates. Since the shift is small in that temperature range (<4 meV between 0 K and 60 K), a high-precision experimental technique is indispensable.

To obtain reliable parameters for the contributions to the gap shift, an appropriate fitting function is required. Several fit formulas for the approximate description of the band-gap temperature dependence can be found in the literature. Very well known and widely used is the Varshni equation,[7] which is a good approximation at high temperatures, but exhibits severe deviations in the low-temperature range. The fitting formula of Manoogian and Wooley[8] tries to separate the two contributions to the band-gap shift, but there are again deviations at low temperatures. The limited validity of these models is demonstrated in Fig. 1 of Ref. 9. A whole series of fitting formulas can be traced to an expression

$$E_g(T)=E_g(0)-\int d(\hbar\omega)\,f(\omega)\,\bar{n}(\omega,T) \qquad (1)$$

with the electron-phonon spectral function[1,5,6,12] $f(\omega)$ and the phonon occupation number $\bar{n}(\omega,T)$. The electron-phonon spectral function is not known *a priori*, and there are two possible ways to obtain one. The theoretically challenging route is to calculate $f(\omega)$ for the semiconductor under investigation taking into account the Debye-Waller and self-energy terms.[1,5,6] There has been considerable progress in these calculations by means of isotopic substitution since the temperature dependence and the mass dependence of the gap are related to each other.[6] However, this approach does not result in a fitting function since there are no free parameters. The second option is to use different functions for $f(\omega)$ leading to the different fitting formulas of Viña *et al.*,[10] O'Donnell and Chen,[11] and Pässler.[9,12] All of these fitting formulas aim at a simple description for the shift of the band-gap energy over the temperature range from below liquid-helium temperature to above room temperature for a whole class of semiconductors.

Experimental temperature-dependent band-gap shift data for one of the best known semiconductor materials, GaAs, have been obtained by a large number of groups. Three articles have attracted considerable interest: Grilli *et al.*[13] reported a high-precision measurement on a bulk GaAs sample, and Oelgart *et al.*[14] as well as Yu *et al.*[15] used multiple quantum wells for their determination of the fundamental gap temperature dependence in bulk GaAs. While Yu *et al.* used the luminescence of the donor bound exciton complex, Grilli *et al.* and Oelgart *et al.* studied the exciton luminescence. Although the samples used in the two latter investigations were of very high quality, all the investigations suffered from two effects. First, the lines broaden considerably even at moderate temperatures (approximately 30 K). Second, the lines are inhomogeneously broadened (see Table II), and higher transitions can contribute to the luminescence line (e.g., the first excited state or the light-hole exciton transition), which complicates the fitting functions for the luminescence line shape.

In this paper, we present an experimental method that allows a high-precision determination of the temperature shift of the band gap. By using spatially resolved photoluminescence spectroscopy (μ-PL), we probe individual excitons strongly localized in GaAs quantum wells. The luminescence

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TABLE I. Properties of the samples used in this investigation.

Name	Layer thicknesses GaAs/AlAs in Å	Number of periods	Growth direction
A	22/23	140	(001)
B	22/23	140	(113)*A*
C	30/28	140	(001)

lines are extremely narrow, and they exhibit no significant broadening up to temperatures around 60 K. Since the lines are homogeneously broadened,[16] we know the line shape *a priori* and are able to obtain the energy of the luminescence peak by a Lorentzian fit very accurately. This accuracy allows us to separate the two contributions to the band-gap shrinkage. In particular, we deduce explicitly the contribution due to electron-phonon interaction.

This paper is organized as follows. After a brief description of the samples and the experimental setup (Sec. II), we explain how to obtain reliable peak position data from the μ-PL spectra (Sec. III). In Sec. IV, we deduce the high-temperature band-gap shift of GaAs caused specifically by electron-phonon interaction. We then compare our results with theoretical predictions.

II. SAMPLES AND EXPERIMENTAL DETAILS

We investigated three GaAs/AlAs superlattices grown by molecular-beam epitaxy. Their layer properties are listed in Table I. Samples *A* and *B* were grown simultaneously on different substrate orientations. Details about the growth and the interface properties of the samples are given in Ref. 17. The global band alignment of the samples is type-II, i.e., the unperturbed conduction-band minimum is in the AlAs and the valence-band maximum is in the GaAs layer. However, layer thickness fluctuations give rise to local changes in the band alignment towards type-I.[18] Those local type-I states are the origin of the aforementioned spectrally narrow luminescence lines we use in this investigation: the electron and hole are here both located in the GaAs slab when recombination occurs.

The experimental setup for μ-PL consists of a He flow cryostat with one thin window. This allows the use of a microscope objective to image (magnification 20×) the excited spot on the sample onto a pinhole. This pinhole defines the spatial resolution as given by the diffraction limit, which in these experiments corresponds to a 2 μm diameter spot. The pinhole is imaged onto the entrance slit of a 0.75 m focal length double grating spectrometer. We use a cooled CCD to record the spectra with a spectral resolution of 30 μeV. The off-resonant excitation source is an unfocused red HeNe laser. The beam strikes the sample under oblique incidence to avoid stray light of, e.g., laser plasma lines. The excitation intensity is kept low (approx. 1 $\mathrm{W\,cm^{-2}}$) to prevent heating of the sample.

III. EXPERIMENTAL RESULTS OF TEMPERATURE-DEPENDENT μ-PL

The idea of using temperature-dependent μ-PL and the sharp radiative transitions to measure the temperature shift of the band-gap energy seems straightforward. Nevertheless, some experimental as well as analytical care has to be taken. We will briefly describe how to obtain reliable data from the measurements.

The most important condition for the experiment is stability. For one, a good temperature stability of the setup is required. We measure the temperature with a diode temperature sensor in good thermal contact with the sample. The temperature is stabilized by the He flow and heating to a fluctuation of less than ± 0.2 K. Another more subtle issue is the spatial stability of the μ-PL. At all temperatures the luminescence must be collected from the same detection spot, which requires elimination of a (thermal) drift of the sample holder. We achieve this by using a circular sample holder which is symmetrically mounted in the cryostat. The sample is mounted in the center of the sample holder. The remaining mechanical drift ($\leqslant 1\ \mu\mathrm{m\,h^{-1}}$) can be eliminated from the spectra, as we only consider narrow lines that can be traced over the whole temperature range under investigation.

A typical μ-PL spectrum is shown in Fig. 1(a). The line shape is dominated by a rather smooth background of type-II luminescence. On this background, spectrally sharp lines are superimposed. The narrow lines on the low-energy side of the zero phonon line [in Fig. 1(a) between 1.82 eV and 1.84 eV] have their origin in localized type-II states,[18] i.e., the electron wave function is located in the AlAs layer. Hence these lines are unsuitable for the current investigation. This is different for the remarkably narrow lines between 1.78 eV and 1.81 eV: narrow luminescence lines in this spectral range stem from localized states formed by a local crossover of the band alignment to type-I.[18] For these states, both electron and hole are situated in the GaAs layer. The narrow lines in this spectral range are so few that it is possible to trace them individually. To illustrate this by an example, one line is traced in Fig. 1(b). Some lines are energetically very close. To avoid ambiguities from multiple peak fits, we pick only lines that are clearly isolated.

After choosing a suitable line from the temperature-dependent μ-PL spectra, we subtract the underlying background line shape, which is about one order of magnitude lower in intensity. We fit the remaining homogeneously broadened line with a Lorentzian line shape. An example for a fitted temperature series is shown in Fig. 2. Note that the fits extend over almost two orders of magnitude in intensity. If the Lorentz fit is not good for all lines in one temperature series, the series is discarded.

The resulting transition energy measurements are very precise. First, the linewidths [full width at half maximum (FWHM)] are always less than 200 μeV, even at 60 K. This should be compared with the order-of-magnitude larger linewidths in most previously reported experiments (Table II). Second, since we know the line shape of the narrow lines *a priori*, the accuracy of the peak energies obtained from the Lorentzian fit is always <5 μeV standard deviation (and typically even <1 μeV).

The use of homogeneosly broadened lines (i.e., emission of *single* localized excitons) eliminates one source for systematic errors present in investigations of inhomogeneously broadened luminescence lines (i.e., emission of an *ensemble* of excitons). In the case of an inhomogeneously broadened luminescence line, chances are high that the excitons are not

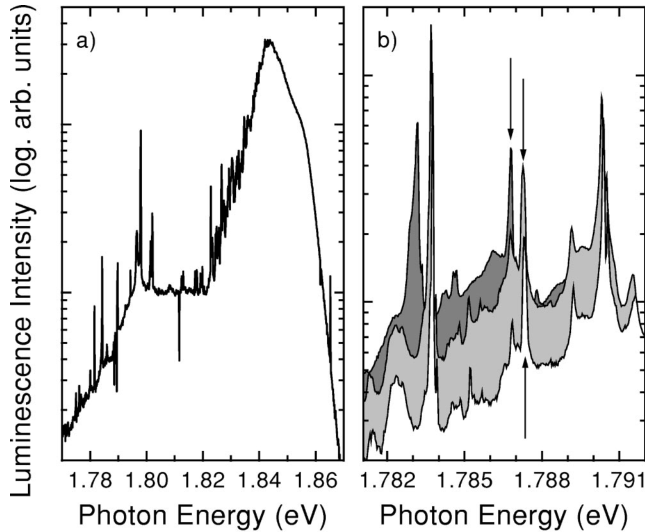

FIG. 1. (a) A typical μ-PL spectrum obtained for sample A at 25 K on a logarithmic scale. Superimposed on a smooth background are several spectrally narrow lines between 1.78 eV and 1.81 eV which are higher in intensity by aproximately one order of magnitude. (b) Expanded view of several lines at 10 K (white), 15 K (light gray) and 30 K (dark gray). Of these, only the one marked by the arrow is considered suitable for investigation.

free but localized. A redshift of the luminescence line with higher temperatures can therefore result not only from the change of the band gap with temperature, but also from a redistribution of the ensemble within the localized states due to thermally activated transport. In the case of homogeneously broadened lines, this thermally activated transport is still possible, but it does not affect the spectral position of the sharp emission lines. The luminescence lines simply vanish due to the delocalization processes. As a result, the experimental error (see Table II) is smaller by one to two orders of magnitude compared to Refs. 13–15.

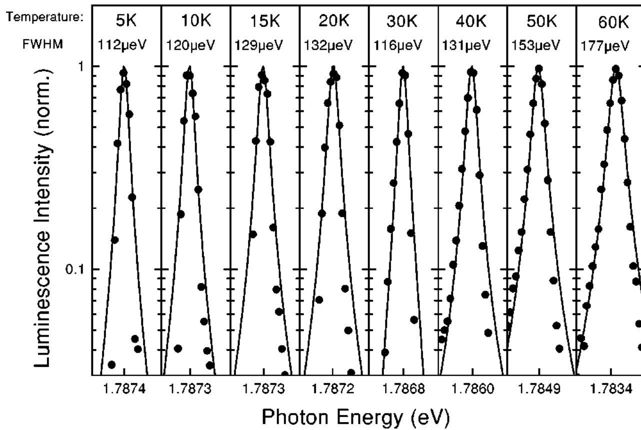

FIG. 2. After extraction from the raw spectra, the narrow lines are fitted by a Lorentzian line shape. The good agreement of the fit with the data confirms that the lines are homogeneously broadened. In each subfigure, which covers a photon energy range of 800 μeV, we give only a rough number for the peak photon energy. The accuracy of the peak position from the Lorentzian fit is much better, typically with a standard deviation of 1 μeV.

TABLE II. Comparison of the luminescence linewidths and experimental uncertainties of the peak positions from Refs. 13–15 and from this work. The listed values from Ref. 14 refer to the heavy-hole exciton transition. For Ref. 15, the FWHM at 60 K cannot be stated since in the spectrum at 80 K the D^0X_{1h} and D^0X_{1l} emission lines already merge; further, the experimental uncertainty is merely assumed since it is not stated explicitly in the paper. For the present investigation, we give upper limits for the linewidths obtained for nine lines in three different samples.

FWHM at		Experimental uncertainty	
5 K	60 K	of peak position, $\Delta\hbar\omega$	Ref.
1.5 meV	*	assumed 300 μeV	15
1.4 meV	$\approx$2 meV	$\leqslant\pm$300 μeV	14
0.7 meV	$\approx$2 meV	$\approx\pm$300 μeV	13
$<$0.15 meV	$<$0.2 meV	$\leqslant\pm$5 μeV	this work

IV. ANALYSIS AND DISCUSSION

We have already mentioned that the temperature dependence of the band-gap energy in a bulk semiconductor is caused by two independent contributions, namely the effect of thermal expansion of the crystal and the electron-phonon interaction. Since we investigate low dimensional structures, the change of the confinement energy due to thermal expansion of the quantum well is an additional contribution to the transition energy shift. The temperature dependence can be written accordingly as

$$\Delta E(T)=\Delta E_{\text{el-ph}}(T)+\Delta E_{\text{lattice}}(T)+\Delta E_{\text{conf}}(T). \quad (2)$$

For the change in the confinement energy, we can easily give an upper limit. Assuming infinite barrier heights and well widths L_z, we overestimate the shift and obtain

$$|\Delta E_{\text{conf}}(T)|\leqslant 2\,E_{\text{conf}}(T=0\text{ K})\times\frac{\Delta L_z}{L_z} \quad (3)$$

$$=2\,E_{\text{conf}}(T=0\text{ K})\times\frac{1}{3}\int_0^T\alpha_V(T')\,dT' \quad (4)$$

$$\leqslant 2\times 500\text{ meV}\times 4\times 10^{-6}=2\ \mu\text{eV} \quad (5)$$

in the temperature range 0 K to 60 K. Here, $\alpha_V(T)$ is the volume expansion coefficient of GaAs.[19] Since this change is not detectable within our spectral resolution, we can safely disregard it in the further analysis.

The lattice contribution (or the implicit part of the band-gap shift) is given by[2]

$$\Delta E_{\text{lattice}}(T)=-B\frac{dE}{dp}\int_0^T\alpha_V(T')dT', \quad (6)$$

where $B=0.77$ Mbar denotes the bulk modulus of GaAs,[19] and $dE/dp=10.7\text{ eV Mbar}^{-1}$ is the pressure-induced band-gap shift.[20] The energy shift $\Delta E_{\text{lattice}}(T)$ has its maximum around 50 K, and it is always smaller than 100 μeV [dashed line in Fig. 3(a)]. Although this contribution is small and amounts to approximately 3% of the band-gap shift in the

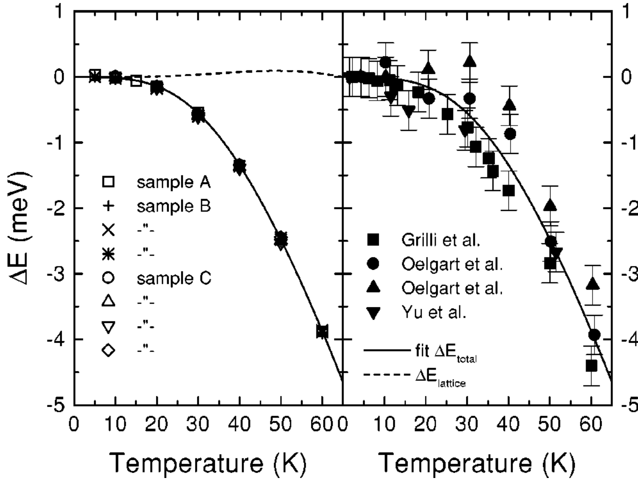

FIG. 3. (a) Data points for all samples used in this investigation. The data points for different samples nearly coincide. The solid line is a fit curve for one of the data sets, where both electron-phonon interaction and lattice expansion have been taken into account. The dashed line represents the contribution of the lattice expansion alone to the change of the band gap. (b) The data points of Refs. 13–15 scatter around the fitting function used in (a) within their error bars.

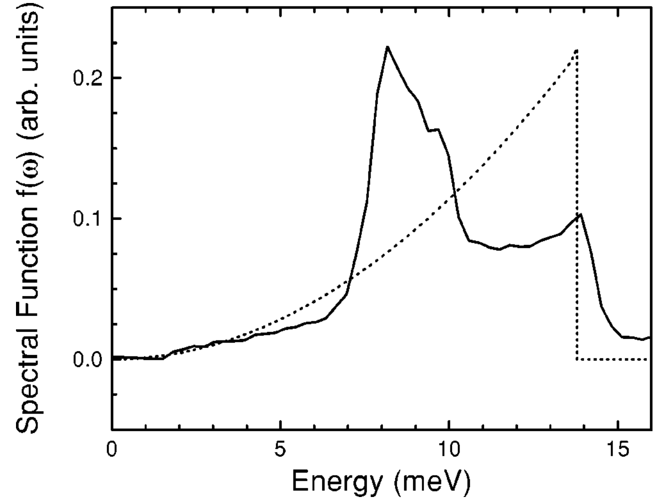

FIG. 4. Solid line: calculated electron-phonon spectral function for GaAs (Ref. 5). Dashed line: electron-phonon spectral function used in this paper to fit the temperature-dependent band-gap shift.

relevant temperature range, we take it into account when we fit the explicit electron-phonon interaction theory to the experimental data.

The general relation for calculating the temperature-dependent contribution due to electron-phonon interaction is given by an integral of the form[1,9,12]

$$\Delta E_{\text{el-ph}}(T)=\int_0^\infty d(\hbar\omega)\,f(\omega)\bar{n}(\omega,T). \tag{7}$$

In this expression, $\bar{n}(\omega,T)$ represents the average phonon occupation number (Bose-Einstein distribution), and $f(\omega)$ is the electron-phonon spectral function.[1] This function is not known *a priori*. Pässler[9,12] uses a variety of electron-phonon spectral functions to obtain different fit formulas. The choice of $f(\omega)$ seems thus quite arbitrary. However, Collins suggests[21] that the spectral function is proportional to a product of the density of phonon states (DOS) and the phonon energy,

$$f(\omega)\propto\omega\times\mathrm{DOS}(\omega). \tag{8}$$

We use this approach here and simplify the DOS with the Debye model. This can be justified *a priori* since the temperature range under investigation is well below the Debye temperature of $\Theta_D>240$ K (see discussion in Ref. 19). An *a posteriori* justification is also available and will be discussed later. The resulting electron-phonon spectral function is[22]

$$f(\omega)=3\frac{a}{k_B}\left(\frac{\omega}{\omega_0}\right)^3. \tag{9}$$

The integration is truncated at the cutoff energy $\hbar\omega_0$. Using the notation of Ref. 9, this energy can be translated into an effective temperature by $\hbar\omega_0=\frac{3}{4}k_b\Theta_0$. The parameter a represents the high-temperature linear asymptote of the band-gap change,

$$a=\lim_{T\to\infty}\frac{dE}{dT}. \tag{10}$$

But, it is important to note that this analysis of the low-temperature range *is nearly exclusively sensitive to changes caused by the electron-phonon interaction.* This is different from measurements at high temperatures, where the lattice expansion and the electron-phonon interaction contribute almost equally to the band-gap shift. Therefore, previous investigations were sensitive to the combined effect.

From our fit to all data sets, we obtain the parameters

$$a=(198^{+5}_{-8})\ \mu\mathrm{eV\,K^{-1}}, \tag{11}$$

$$\hbar\omega_0=(13.8^{+0.2}_{-0.3})\ \mathrm{meV}\Leftrightarrow\Theta_0=(120^{+2}_{-3})\ \mathrm{K}. \tag{12}$$

The standard deviation $\sqrt{\chi^2}$ of the fit to each temperature series is very small, typically about 15 μeV. All data points of the present investigation are plotted with the fitting function in Fig. 3(a), and the data of Refs. 13–15 are plotted for comparison in Fig. 3(b). From Fig. 3, three important conclusions can be drawn. First, the measurements presented here have a very good accuracy. The data points for different samples almost coincide. The measured energy shift is the same for both the (001) and the (113)A growth directions. This is expected since the temperature-dependent band-gap shift is a material parameter of GaAs which is independent of the crystal orientation. Second, the fitting function [Eqs. (7) and (9)] seems appropriate, as it reproduces the temperature dependence very accurately. Using the fitting formulas of Varshni or Viña results in much higher $\sqrt{\chi^2}$ values. We can therefore justify *a posteriori* that the approach for the electron-phonon spectral function is good. If we plot the calculated electron-phonon spectral function for GaAs (Ref. 5) with the one used here (Fig. 4), we find a resonable value for the cutoff energy $\hbar\omega_0$. The next peak in the spectral function is at much higher energies and results from the longitudinal acoustic zone boundary phonons. Third, the data of Refs. 13–15 scatter around the fitting function [Fig. 3(b)] within

their error bars, which confirms that the previous data agree with the measurements presented here.

The experimental values in the literature for the slope of the high-temperature asymptote of the band-gap shift obtained in the temperature interval [100 K, 300 K] are in the range between $-370\,\mu\mathrm{eV\,K}^{-1}$ and $-395\,\mu\mathrm{eV\,K}^{-1}$.[23] These values contain both the contribution from electron-phonon interaction and lattice expansion. The contribution due to lattice expansion calculated[2] with Eq. (6) is $(dE_g/dT)_{\mathrm{lattice}} = -170\,\mu\mathrm{eV\,K}^{-1}$. This leads to values for a between $-200\,\mu\mathrm{eV\,K}^{-1}$ and $-225\,\mu\mathrm{eV\,K}^{-1}$. However, this determination of the electron-phonon contribution is very indirect, and there are a lot of uncertainties. On the other hand, our experimental determination of $a=(-198^{+5}_{-8})\,\mu\mathrm{eV\,K}^{-1}$ is direct and very precise.

V. CONCLUSION

We have used temperature-dependent μ-PL of GaAs/AlAs heterostructures for high-precision measurements of the band-gap shift in GaAs. We have determined the contribution to the change in the band-gap energy due to electron-phonon interaction. We have given evidence that the suggestion[21] for the electron-phonon spectral function $f(\omega)=\omega\times\mathrm{DOS}(\omega)$ is a good approximation.

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