Evidence of two disorder scales in Ga(AsBi)

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Temperature-dependent photoluminescence in a Ga(AsBi) structure is modelled in an excitonic hopping model and compared to experiment. It is shown that theory and experiment cannot be brought into agreement when using a single energy scale. Thus, a second energy scale is introduced, resulting in a good agreement between theory and experiment. The two scales are identified with spatially large alloy disorder and additional cluster states subdividing this first scale.

1 Introduction Ga(AsBi) has been intensively discussed as an attractive candidate for laser applications in the near and mid infrared wavelength region recently. This is primarily due to the fact that the incorporation of Bi into GaAs strongly reduces the band gap between 60 and 80 meV per percentage Bi [1–4]. Recent results show that the band structure of Ga(AsBi) can be described by a band anticrossing model of the valence band. This is in marked contrast to the more prominent dilute nitride system where anticrossing occurs in the conduction band [5].

Ga(AsBi) is still difficult to grow due to the high lattice missmatch, the metallic character of GaBi and the low electronegativity of Bi. It is, however, possible to grow high quality Ga(AsBi) crystals containing up to 10% Bi using molecular beam epitaxy growing techniques [6–8].

Ga(AsBi) as a new material with the above described fabrication problems is heavily influenced by disorder effects which manifest themselves in spatial fluctuations of the Bi concentration. These lead to variations of the band gap and in term to a broadend density of localized states (DOS) at the low energy tail. Since the conduction band is almost unaffected by the Bi atoms, the localized states are only present in the valence band.

Photoluminescence (PL) offers a good possibility to characterize the optical properties of semiconductor materials. PL spectroscopy gives access to the optical and electronic properties of semiconductor materials. In the low density regime, the PL of disorderd semiconductors can be described by the hopping of excitons among localized states [9]. In this publication, we concentrate on the temperature-dependence of PL characteristics such as the emission energy and the full width at half maximum (FWHM) of the resonance. We show that these may be well represented by an excitonic hopping model, where, however, a second energy scale has to be introduced for an exhaustive description of the phenomena.

2 Experimental results The investigated sample is a 30 nm thick molecular beam epitaxy-grown Ga(AsBi) layer containing 4–5% Bi. The Ga(AsBi) layer is contained between a 450 nm GaAs buffer layer on GaAs substrate and a 300 nm GaAs capping layer. Details concerning sample growth can be taken from Ref. [8].

The linear absorption representing the DOS of our sample is shown in Fig. 1 and yields a band gap of 1.19 eV. For the sake of clarity we also show the PL spectrum of our sample. The inset of Fig. 1 shows the linear absorption on a logarithmic scale which makes clear that one obtains a Gaussian-shaped low energy tail of the DOS.

Figure 2a shows the temperaure-dependent Stokes-shift. The Stokes-shift, which is the difference of the PL peak position and the fundamental bandgap, is deduced from the measured temperature dependent PL and the zero-temperature band gap taken from the linear absorption spectrum. We assume the PL peak position to fit with a Varshni function ($E_g(T) = E_{g,0} - \alpha T^2/(\beta + T)$) in the high temperature regime [10]. As Varshni parameters, we obtain
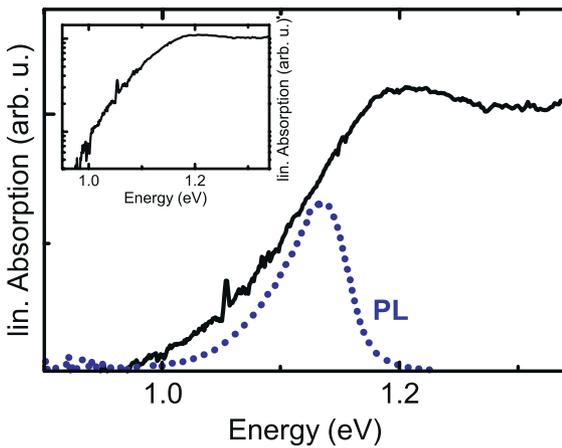
Figure 1 (online color at: www.pss-b.com) Linear absorption (solid line) and PL (blue dots) at an excitation power $P = 2.5$ mW of the Ga(AsBi) sample at 10 K. Inset: Linear absorption on a logarithmic scale which shows a Gaussian shaped low energy tail, suggesting the use of a Gaussian density of states in the following exciton hopping calculation.
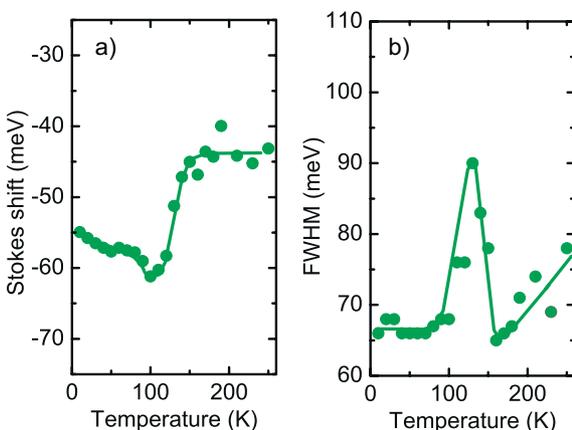
$\alpha = 0.274$ meV/K and $\beta = 468$ K and the zero-temperature bandgap $E_{g,0}$ is taken from the linear absorption spectrum, $E_{g,0} = 1.19$ eV. The temperature dependence of the Stokes-shift shows a so-called "s-shape" behavior, which means that with increasing temperature the Stokes-shift first increases up to a temperature of $T = 120$ K and then decrases up to a temperature of $T = 150$ K. For higher temperatures the Stokes-shift remains at a constant amount ($\Delta E_{st} \approx 45$ meV) because we assumed the PL peak position to follow the bandgap when fitting the Varshni parameters. This large Stokes-shift shows that the PL of the sample is dominated by disorder effects even at high temperatures ($T > 150$ K). The temperature-dependent FWHM which is also shown in Fig. 2 shows a maximum at 140 K, which is a typical indication of an exponential DOS. This is easily understandable in the limit of an infinite lifetime because the PL spectrum is governed by the product of the DOS and the Boltzmann function at a given temperature. If the energy dependence of the DOS is weaker than that of the exponential function, the distribution is mainly determined by the Boltzmann function, whereas if it is stronger, e.g., Gaussian, the DOS energy dependence takes over. Our calculations show that the argument also holds for realistic radiative decay times, displaying a maximum in the energy dependence of the FWHM for an exponential DOS (Fig. 3b) but not for a Gaussian DOS (Fig. 4b).

3 Simulation results

Single energy scale approach The kinetic Monte-Carlo simulation of exciton hopping has been applied to many semiconductor materials, e.g., (GaIn)(NAs) [11]. In this theory, disorder parameters may be extracted directly from the temperature-dependent PL spectra. The parameters entering the theory are $N_0\alpha^2$ where N_0 is the area DOS and α the exciton localization radius, $\nu_0\tau_0$ where ν_0 is the Debye-frequency and τ_0 the exciton lifetime, and the DOS with its characteristic energy scale ε_0. The DOS is described by a

Figure 2 (online color at: www.pss-b.com) (a) Temperature dependence of the Stokes shift of the Ga(AsBi) sample at an excitation power $P = 2.5$ mW. (b) Temperature-dependent FWHM.
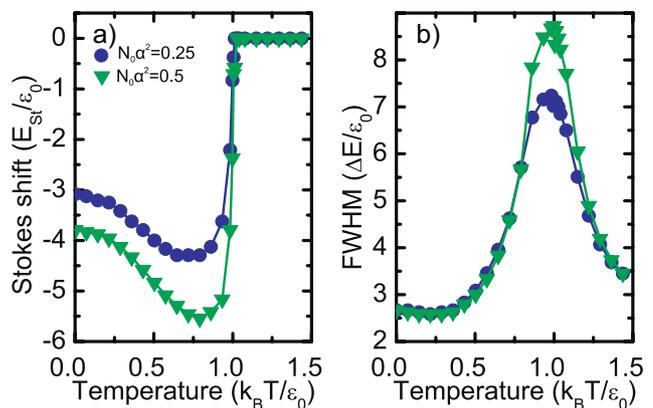
Figure 3 (online color at: www.pss-b.com) Temperature dependence of the Stokes-shift (a) and the PL linewidth (b) for $N_0\alpha^2 = 0.25$ (circles) and $N_0\alpha^2 = 0.5$ (triangles), $\nu_0\tau_0 = 10^4$, and a characteristic energy scale $\varepsilon_0 = 12$ meV using an exponential DOS.

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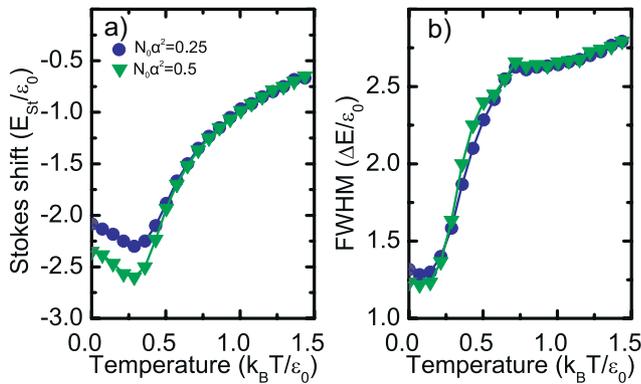
Figure 4 (online color at: www.pss-b.com) Simulation results for the temperature-dependent Stokes-shift (a) and PL linewidth (b) for $N_0\alpha^2 = 0.25$ (circles) and $N_0\alpha^2 = 0.5$ (triangles), $\nu_0\tau_0 = 10^4$ and a characteristic energy scale $\varepsilon_0 = 12$ meV using a Gaussian DOS.

specific distribution function which in the past turned out to generally be an exponential function for quantum wells and a Gaussian distribution for bulk systems. Details of the algorithm can be found in Ref. [9].

As was done in previous publications, e.g., Ref. [11], we assume that disorder within the material can be described by a single characteristic energy scale ε_0. Because of the observed maximum in the temperature-dependent FWHM, see Fig. 2, the shape of the DOS is taken as an exponential function:

$$g(\varepsilon) = \frac{N}{\varepsilon_0}\exp\left(\frac{-\varepsilon}{\varepsilon_0}\right). \tag{1}$$

We calculate the temperature dependent PL for two typical parameter sets using $N_0\alpha^2 = 0.25$ and $N_0\alpha^2 = 0.5$, $\nu_0\tau_0 = 10^4$, and a characteristic energy scale of $\varepsilon_0 = 12$ meV. The corresponding Stokes shift is plotted in Fig. 3a and the PL linewidth in Fig. 3b. For the determination of the latter, a Boltzmann distribution above the bandgap was added to model the continuum range. We obtain an "s-shape" behavior of the PL maximum with a maximum around $k_BT = 0.8\,\varepsilon_0$ the height of which depends on $N_0\alpha^2$. The Stokes shift vanishes for temperatures $k_BT > \varepsilon_0$. The PL linewidth has a maximum around $k_BT = 1.0\,\varepsilon_0$ and shows no dependence on $N_0\alpha^2$ at $T = 0$. These results are consistent with previous results, see, e.g., Ref. [11, 12]. In order to reproduce the experimental data shown in Fig. 2, we can extract the characteristic energy scale by comparing specific points which are independent of $N_0\alpha^2$ and $\nu_0\tau_0$ [11]. The comparison of the maximum Stokes-shift and the maximum PL linewidth yields a characteristic energy scale between 11 and 15 meV. As is visible in Fig. 3, the zero-temperature FWHM for an exponential DOS is independent of the specific parameters and lies in the range of $2.4\varepsilon_0$. Using the above-cited $\varepsilon_0 = 10$–15 meV, we are led to an FWHM of 24 meV up to 36 meV whereas the experimental value is around 70 meV. In addition, we find a non-vanishing Stokes

shift at high temperatures in the experiment which can also not be explained with the approach of an exponential DOS since the Stokes-shift vanishes for temperatures $k_BT > \varepsilon_0$. Furthermore, the measurements show a Gaussian-shaped low energy tail of the absorption spectrum which should represent the DOS, see Fig. 1, in marked contrast to the exponential DOS we have been using due to the measured maximum in the temperature-dependent FWHM, see Fig. 2.

In a second attempt to reproduce the experimental data, we assume a Gaussian-shaped DOS described by

$$g(\varepsilon) = \left(\frac{N^2}{2\pi\varepsilon_0^2}\right)^{\frac{1}{2}}\exp\left(-\frac{\varepsilon^2}{2\varepsilon_0^2}\right), \tag{2}$$

which, using the same parameters $N_0\alpha^2$ and $\nu_0\tau_0$ as for the previous calculation with an exponential DOS and a characteristic energy scale of $\varepsilon_0 = 12$ meV, yields the Stokes-shift and PL linewidth shown in Fig. 4. Again, we compare the experimental data with the calculated spectra at specific points which are independent of or show only slight dependence on $N_0\alpha^2$ and $\nu_0\tau_0$ [9, 12]. We obtain the maximum Stokes-shift around $k_BT \approx 0.3\,\varepsilon_0$ which yields $\varepsilon_0 \approx 30$ meV. The zero-temperature PL linewidth depends slightly on $N_0\alpha^2$ but is in the range below $1.5\varepsilon_0$ which is inconsistent with the measured data. Besides the wrong energy scales, the temperature dependent PL linewidth does not show a maximum for a Gaussian density of states (Ref. [12]) in marked contrast to the measurements, see Fig. 2.

3.2 Two energy scale approach Since the experimental data shows both indications for a Gaussian DOS (linear absorption spectrum, see Fig. 1) and for an exponential DOS (maximum in PL linewidth, see Fig. 2), we conclude that the disorder of the Ga(AsBi) material system is determined by two energy scales with different DOS. The two energy scales also differ in the magnitude of ε_0, explaining our contradictory results in the previous section. We identify the first scale with alloy disorder caused by fluctuations of the Bi concentration which are spatially large and Gaussian distributed. The second scale is given by additonal cluster sites below the fluctuating band gap which are distributed exponentially. Hence, we describe the disorder for the first scale by a parameter set consisting for the first scale of ε_1, $N_1\alpha_1^2$, and $\nu_1\tau_1$, where τ_1 is now not the exciton lifetime anymore but rather the relaxation time for transitions to the cluster states of the second energy scale. For the second scale, parameters are denominated ε_2, $N_2\alpha_2^2$, and $\nu_2\tau_2$. Details for the model of two energy scales and an excitation-power-dependent discussion of the PL spectra can be found in Ref. [13]. Figure 5 shows the calculated Stokes-shift (a) and FWHM (b) using the approach of two energy scales and the parameters $N_1\alpha_1^2 = 0.01$, $\nu_1\tau_1 = 10e^5$, $\varepsilon_1 = 45$ meV, $N_2\alpha_2^2 = 0.15$, $\nu_2\tau_2 = 10^4$, and $\varepsilon_2 = 11$ meV. We now obtain a very good agreement between the experiment and theory. The discrepancy between
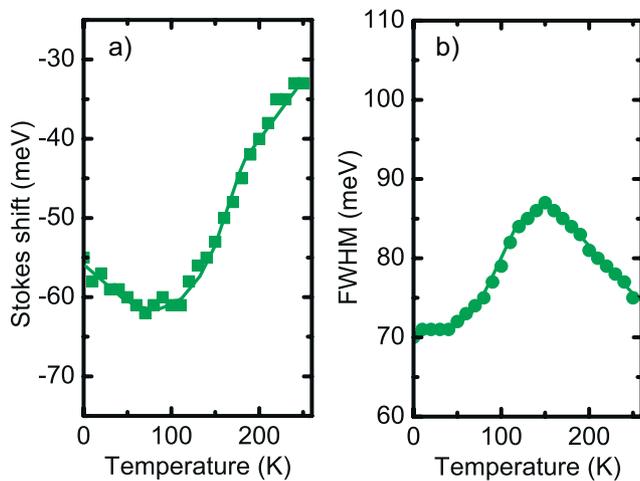
Figure 5 (online color at: www.pss-b.com) Simulation results of the temperature dependent Stokes-shift (a) and PL linewidth (b) for $N_1\alpha_1^2 = 0.01$, $\nu_1\tau_1 = 10e^5$, $\varepsilon_1 = 45$ meV, $N_2\alpha_2^2 = 0.15$, $\nu_2\tau_2 = 10^4$, and $\varepsilon_2 = 11$ meV using the model of two energy scales.

experiment and theory in the high order temperature range can be attributed to the not well-known Varshni-parameter of Ga(AsBi) for the Stokes-shift and to deviations from the exponential and Gaussian DOS of the localized sites for the PL linewidth.

3 Conclusion We have presented temperature-dependent measurements of the PL peak position and linewidth in a Ga(AsBi) structure. The measurements show indications of two different energy scales as well as of an exponential and a Gaussian density of states. Attempts to reproduce the experiment in a single-scale excitonic hopping simulation have been shown to fail. We conclude that two disorder energy scales, one with an exponential and one with a Gaussian density of states, are necessary to model the measurements. The two scales are identified with a large-scale alloy disorder distribution and cluster states

subdividing this large scale. The corresponding calculation shows good agreement with experiment.

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