Clustering effects in Ga(AsBi)

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The photoluminescence from a Ga(AsBi) sample is investigated as a function of pump power and lattice temperature. The disorder-related features are analyzed using a Monte Carlo simulation technique. A two-scale approach is introduced to separately account for cluster localization and alloy disorder effects. The corresponding characteristic energy scales of 11 and 45 meV are deduced from the detailed comparison between experiment and simulation. © *2010 American Institute of Physics*. [doi:10.1063/1.3374884]

The experimental and theoretical study of bismuth-(Bi-) containing semiconductors has attracted increasing interest over the past few years, mainly due to the giant band gap reduction by as much as 60–80 meV/% Bi.[1–4] In contrast to the well established dilute nitride system,[5] the valence band rather than the conduction band is affected by the incorporation of Bi atoms in GaAs.[6] Ga(AsBi) is a suitable and promising candidate for GaAs-based laser diodes emitting in the near and middle infrared wavelength-region with the possibility of an independent valence band engineering.

Recent investigations show that Bi incorporation results in a huge shift of the split-off band, offering further opportunities for the design of spintronic devices.[7] The Bi atoms are incorporated into GaAs as isovalent impurities due to their electronegativity and ionization energy being significantly lower than those of As. The impurities lead to the dispersionless Bi band below the valence band edge which couples to the valence bands of GaAs yielding mixed states. It is currently assumed that the band structure of Ga(AsBi) is described by a band anticrossing model for the valence band.[8]

Despite the metallic character of GaBi and the high lattice mismatch between GaAs and GaBi,[9] it is possible to grow high quality Ga(AsBi) crystals containing up to 10% Bi.[10] However, disorder effects are always present in compound materials due to fundamental thermodynamics.[11] Spatial fluctuations of Bi concentration result in fluctuations of the band gap, yielding a broadened density of states (DOS) with localized states on the low energy side.[12] This disorder predominantly influences the valence band states since the conduction band is barely affected by the Bi atoms.

Photoluminescence (PL) measurements provide an excellent way to investigate disorder properties avoiding special preparation and/or damage of the sample. Empirical theoretical models have been developed to deduce details of the disorder properties from the PL measurements via kinetic Monte Carlo simulations. The algorithm is generally used to describe the dynamics of excitons and is discussed in Ref. 13. This approach has been applied to characterize disorder effects in a variety of materials, e.g., (GaIn)(NAs)/GaAs quantum wells.[14,15]

The electron-hole pairs in the presented two-dimensional model are treated as excitons in the case of relatively low excitation densities and temperatures. The valence band disorder results in a landscape of localized states between which the individual excitons perform phonon-assisted transitions, so-called hops. The corresponding hopping rate from an occupied state i with energy E_i to an unoccupied state j with energy E_j is given by,

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha} - \frac{E_j - E_i + |E_j - E_i|}{2k_B T}\right), \tag{1}$$

where ν_0 is the attempt-to-escape frequency, r_{ij} is the distance between both sites, α is the exciton localization radius, k_B is the Boltzmann factor, and T is the lattice temperature.[16] The localized states are randomly distributed in space while their energy is given by the distribution function $g_{\epsilon_0}(\epsilon)$. The characteristic energy scale ϵ_0 represents the low energy tail of the DOS which often is assumed to be exponential.[13,14]

A transition between two sites usually involves two or more phonons if the characteristic energy scale exceeds the Debye energy. The transition rate for such multiphonon processes is introduced phenomenologically by extending Eq. (1) by a factor $\exp(-|E_j - E_i|/\hbar\Omega_{\mathrm{LO}})$;[17] the optical phonon energy used is $\Omega_{\mathrm{LO}}=36$ meV, the value of the GaAs host material. The PL spectra are then obtained by simulating the transitions of the excitons between the localized states followed by the radiative decay of the exciton within a characteristic lifetime τ_0. Generally, the PL spectra only depend on $\nu_0\tau_0$, the DOS shape, and $N_0\alpha^2$, where N_0 is the areal density of sites.[13] The parameter $N_0\alpha^2$ is used as an approximation to describe the excitation power dependence in the experiment:

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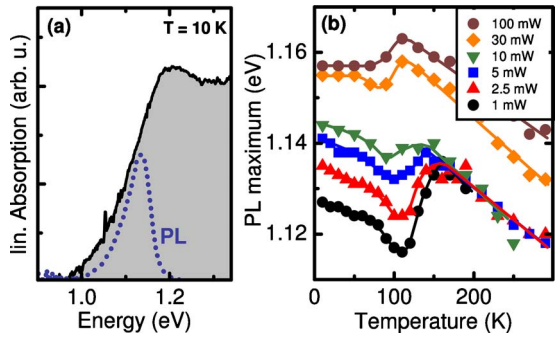

FIG. 1. (Color online) (a) Linear absorption at $T=10$ K and PL spectrum for $P=2.5$ mW. (b) Experimental results for the temperature dependent PL peak position at various excitation intensities.

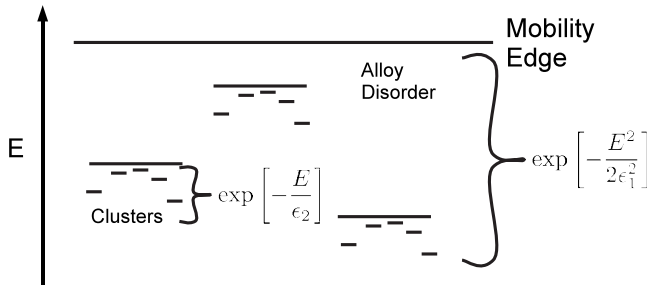

FIG. 2. Hopping on two energy scales. The first one is given by a Gaussian distribution with the characteristic energy scale ϵ_1 and the second scale is given by an exponential distribution with energy scale ϵ_2, representing alloy disorder and cluster localization, respectively.

the sites become filled for higher excitation powers and the number of possible hopping transitions is reduced due to the restriction of only one exciton per site.

All our experimental data were taken on a 30 nm thick layer of Ga(AsBi) with a Bi concentration of about 4%–5%, grown on a GaAs substrate. The corresponding growth details are given in Ref. 10. The quasiresonant PL experiments were performed using 100 fs pulses centered at 1.38 eV below the band gap of the substrate. The PL signal was dispersed by a spectrometer and detected by a streak camera in the time-integrated regime as a function of temperature and excitation density. An excitation power of 1 mW corresponds to the transmitted photon flux at the sample surface of 1.5×10^{12} cm^{-2} s^{-1}. The linear absorption was measured in a standard transmission geometry using a tungsten lamp and a spectrometer with a cooled (GaIn)As photodiode array.

Figure 1(a) shows the linear absorption spectrum of the Ga(AsBi) sample at low temperatures. One clearly observes a strongly broadened exciton signature at 1.19 eV and a pronounced Gaussian band tail at low energies. The corresponding PL spectrum at low excitation density is shown for comparison. The PL maxima are plotted in Fig. 1(b) for various excitation powers between $P=1$ and 100 mW as a function of temperature. The temperature shift of the PL peak deviates strongly from that of an ideal semiconductor exhibiting a so-called "s-shape" typical for a disordered crystal.[14] The Stokes shift is deduced from the PL peak position as follows: the zero-temperature band gap $E_g(T=0)=1.19$ eV is given by the linear absorption spectrum. The temperature dependence of the band gap for $T>150$ K is assumed to follow Varshni's law[18] $\Delta E_g(T)=aT^2/(b+T)$ with $a=0.274$ meV/K and $b=468$ K (fit to experiment).

The deduced Stokes-shift of the Ga(AsBi) sample is shown in Fig. 3(a) showing the typical "s-shape" for low temperatures. A finite Stokes-shift of $\Delta E_{st}=45$ meV is still present even at temperatures $T>150$ K. Thus, the PL spectra are dominated by disorder effects even at these higher temperatures. This is further supported by the strong blueshift of the PL emission at elevated excitation densities of $P=30$ and 100 mW. The same effect is also observed in continuous wave PL at room temperature.[10]

The corresponding full width at half maximum (FWHM) for all PL spectra is plotted in Fig. 3(c). All curves exhibit a maximum at a temperature around $T=130$ K with some dependence on the excitation power. Such a pronounced maximum in the PL line width accompanying the "s-shape" is a typical feature of an exponential density of the localized states.[19]

A standard hopping model with a single energy scale cannot account for our experimental observations. If we were to use such a standard hopping model for the analysis we would assume a single exponentially varying energy scale ϵ_0 for the DOS. The largest Stokes shift would occur around $k_BT \approx 0.6-0.8\epsilon_0$ and the maximum of the FWHM is around $k_BT \approx 1.0-1.2\epsilon_0$, almost independent of $N_0\alpha^2$ and $\nu_0\tau_0$ according to the relation between PL peak position, line width, and the characteristic energy scale ϵ_0.[14] Comparing these points with our experimental results, we then obtain $\epsilon_0 \approx 11-15$ meV. However, the FWHM at zero temperature is $\Delta_{T_0} \approx 2.5\epsilon_0$, which is independent of $N_0\alpha^2$ and $\nu_0\tau_0$. The observed experimental value is around 70 meV and thus yields the characteristic energy scale $\epsilon_0 \approx 28$ meV—almost double the value deduced from the Stokes shift analysis. Further discrepancies are the broad, Gaussian-shaped low energy shoulder in the linear absorption and the nonvanishing Stokes shift at temperatures above $T>120$ K.

To improve the analysis, we therefore extend the standard one-scale picture, introducing a second energy scale. This concept is motivated by the fact that Bi clusters are likely to exist in this system.[20] These clusters act as localization sites for the excitons. The proposed energy distribution of sites is shown schematically in Fig. 2. Potential fluctuations caused by varying Bi concentration are represented by the randomly distributed sites with a large localization length. The corresponding DOS is described by a Gaussian, in agreement with the linear absorption data. The model parameters are $N_1\alpha_1^2$, $\nu_1\tau_1$, and an energy scale ϵ_1. For every spatially large site, we have additional smaller sites, lower in energy and again randomly distributed. These sites represent the Bi clusters. The DOS of this second scale is assumed to be exponential and is characterized by $N_2\alpha_2^2$, $\nu_2\tau_2$, and ϵ_2. The revised Monte Carlo algorithm runs as follows: In a first step, the exciton performs transitions between the sites of the first energy scale, reflecting alloy disorder. The relaxation time τ_1 now expresses not decay but rather the transition to the second energy scale where the exciton starts hopping among the cluster sites.

Using the two-scale model in our kinetic Monte Carlo simulation we now obtain the temperature dependence of the Stokes-shift and the FWHM of the PL shown in Figs. 3(b) and 3(d). Excellent agreement with the experimental data in Figs. 3(a) and 3(c) is found, nicely reproducing all the main characteristics of the PL temperature and density dependence. Furthermore, the PL lineshapes are correctly repro-

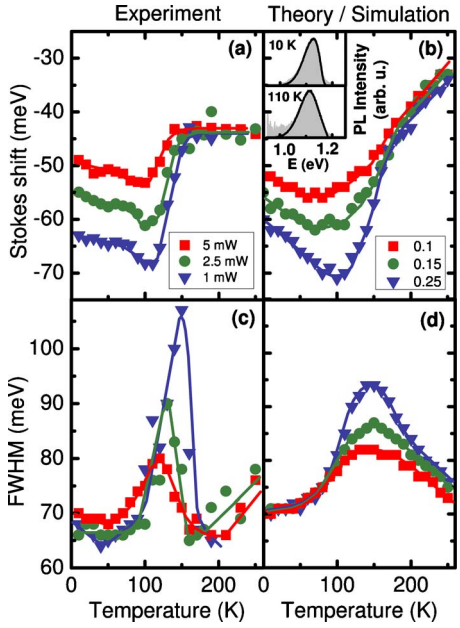

FIG. 3. (Color online) Left: Experimental Stokes shift (a) and FWHM (c) for varying excitation powers. Right: Calculated Stokes shift (b) and FWHM (d) for varying $N_2\alpha_2^2$ using the two-scale model. Energy scales of $\epsilon_1 = 45$ meV and $\epsilon_2 = 11$ eV are obtained. The inset in (b) shows experimental (gray area) and theoretical (black line) PL spectra for the temperatures of 10 and 110 K at the excitation density of 1 mW.

duced [inset of Fig. 3(b)]. To obtain this agreement, we used the parameters $N_1\alpha_1^2 = 0.01$, $\nu_1\tau_1 = 10^5$, $\epsilon_1 = 45$ meV, $\nu_2\tau_2 = 10^4$, and $\epsilon_2 = 11$ meV. The minute remaining differences between theory and experiment are mainly attributed to uncertainties in the temperature dependence of the Ga(AsBi) band gap and the precise distribution of the Bi cluster states.

The kinetic Monte Carlo algorithm also explains the strong temperature dependence of the PL intensity which is often observed in disordered semiconductor materials.[21] Two parameters are important: The DOS, where the exponential distribution with the characteristic energy scale ϵ_2 is used, and the relative density of nonradiative sites given by $N_{nr}/(N_r+N_{nr})$. We assume that an exciton can reach all the nonradiative recombination centers due to the spatially large extension of the sites. Thus, the energy scale $\epsilon_2 = 11$ meV is sufficient in order to explain the PL intensity. Figure 4 gives the experimental and calculated temperature dependence of the normalized PL intensity. Again, a very good agreement between theory and experiment is obtained with the relative density of nonradiative recombination centers of $N_{nr}/(N_r+N_{nr}) = 0.012$ for excitation power $P = 5$ mW and $N_{nr}/(N_r+N_{nr}) = 0.008$ for $P = 10$ mW. Here, we relate $N_{nr}/(N_r+N_{nr}) = 0.012$ to the excitation power due to the restriction of one exciton per localized state.

In summary, the temperature and excitation power dependence of the PL in a $Ga(As_{0.95}Bi_{0.05})$ sample is studied experimentally and modeled using kinetic Monte Carlo simulations. We use a two-scale approach, modeling the alloy disorder and cluster localization separately as an extension of the standard disorder model.[13,14] Excellent agreement between experiment and simulation results is obtained assuming 45 and 11 meV as characteristic energy scales of the alloy fluctuations and the DOS of Bi clusters, respectively.

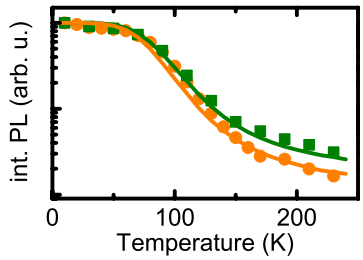

FIG. 4. (Color online) Temperature dependence of the PL intensity. The solid lines represent the simulation and squares/dots show the measured normalized PL intensity for $N_{nr}/(N_r+N_{nr}) = 0.012$ and excitation power $P = 5$ mW (lower curve), and $N_{nr}/(N_r+N_{nr}) = 0.008$ and $P = 10$ mW (upper curve).

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