Luminescent properties of GaAsBi /GaAs double quantum well heterostructures

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Abstract

GaAsBi/GaAs double quantum well (DQW) heterostructures are grown at low temperatures using molecular beam epitaxy without growth interruption and studied by means of high-resolution x-ray diffraction and continuous wave photoluminescence (PL). Line shape analysis of PL spectra measured at various excitation densities allows reveals QW coupling due to tunneling. It is shown that an efficient PL of GaAs/GaAs_{1-x}Bi_x/GaAs DQWs is significantly more thermally stable than that from a single quantum well (SQW) structure of similar composition. Such stabilization is described in terms of carrier redistribution between coupled quantum wells and is caused by carrier capture in the QW, thermal emission, and diffusion in the barrier.

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I. Introduction

Physical properties of dilute $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ heterostructures are of great interest both for fundamental physics [1-8] and for potential device applications [9–14]. Indeed, replacement of a small amount of As by bismuth in GaAs matrix drastically changes electronic and spin states of the material which causes a decrease in band gap (E_g) of up to ~ 90 meV/% of Bi [1, 15, 17] and, an increase of the spin-split-off energy separation, Δ_{SO} , between the valence band edge and the split-off band [9]. The physical origin of observed effects has been suggested to be an anticrossing interaction between Bi-related resonant defect levels and the valence band edge of the GaAs matrix [4, 9]. As a result it has been demonstrated that Δ_{SO} exceeds the E_g value already for $x \sim 9\%$ [18]. This has a beneficial secondary effect of reducing Auger recombination losses in devices used dilute $\text{GaAs}_{1-x}\text{Bi}_x$ material. While such losses are a common problem for telecommunication devices, utilization of GaAsBi alloys could benefit laser diodes operating in the 1.3-1.6 μm spectral range with improved operation efficiency and temperature insensitivity [9, 12, 18]. These and other applications have stimulated extensive recent studies of dilute bismides [19-30]. They could make use of high quality $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ separate confinement heterostructures [14, 31, 32] and multiple quantum wells [31, 33-37] in the active regions. In previous studies, we investigated the effects of AlGaAs cladding on the luminescent properties of $\text{GaAs}/\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ heterostructures [32] where the PL was demonstrated to be substantially more thermally stable PL than an isolated single quantum well (SQW). In this work, we investigate the optical properties of molecular beam epitaxy grown double GaAsBi/GaAs QWs. Here, we use the technique of no growth interruptions, which was shown to improve

interface quality, [31] to show that the DQW $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ samples exhibit strong room temperature photoluminescence (PL) and excellent optical properties.

II. Sample growth and characterization.

Both SQW (sample A) and DQW (sample B) $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ heterostructures for our study were grown on semi-insulating GaAs (001) substrates in a Riber-32P MBE system. In order to monitor the substrate temperature during growth a kSA BandiT optical bandgap thermometer was utilized. The substrate temperature was kept at 320 °C throughout the growth of the GaAsBi QWs, GaAs spacers, and the GaAs cap layers, all of which were grown without interruption. This prevented contamination and improved the interface quality. A (2×1) RHEED reconstruction pattern was observed during the growth of the GaAsBi QWs which changed to a (1×3) pattern for the layers after the QW. Growing procedure is described in detail in Ref. [31].

Preliminary analysis of as-grown structure was performed using high-resolution x-ray diffraction (HR-XRD). The corresponding experimental rocking curves of the symmetric (004) Bragg reflections along with their simulations are shown in Figure 1 for both samples. Pronounced thickness fringes from both samples are observed demonstrating the high quality and long-range coherence of the interfaces. Additionally, x-ray reciprocal space maps in the vicinity of the asymmetric (224) Bragg reflection (not shown) demonstrate that all layers are pseudomorphically (coherently) strained in both samples. The X-ray simulations shown in Figure 1 were carried out in the framework of a quasi-kinematical scattering algorithm [7] which allows a quantitative analysis of the experimental rocking curves. By applying a least-squares fitting procedure the vertical distribution of Bi inside the $\text{GaAs}_{1-x}\text{Bi}_x$ QWs, the corresponding vertical strain profile, which is directly proportional to concentration profile due to the pseudomorphic

growth, and the $\text{GaAs}_{1-x}\text{Bi}_x$ layer thicknesses can be determined from x-ray simulations with high accuracy. The simulations are insensitive to the GaAs buffer, however, they do show that the GaAs layers grown after the GaAsBi QW are slightly vertically strained. The QW parameters found from simulations are presented in Table 1. In particular, we find that in sample A the QW is ~ 3.9 nm thick with $\sim 4.2\%$ Bi, and in sample B the QWs are 4.9 and 5.0 nm thick with 3.0% and 4.0% Bi for the bottom and top layers, respectively (Table 1). GaAsBi layers in sample B are found to be separated by a 6.2 nm thick GaAs layer. In what follows we investigate the optical properties of the DQW sample B through exciton PL in comparison with the SQW reference sample.

III. Experimental results and discussions

PL studies were carried out at different excitation intensities and temperatures. The 532 nm line from a frequency doubled Nd:YAG laser was used as excitation in all cases. The laser power was varied in the range of $\sim (10^{-6} - 10^2)$ mW and focused to a spot with a diameter of ~ 20 μm . The PL signal was dispersed by a 0.5-m single-grating monochromator and detected by a LN-cooled OMA V: InGaAs photodiode detector array. The samples were mounted in a closed-cycle helium cryostat in order to control the temperature between 10 and 300 K.

a) Dependence on excitation intensity.

First, PL spectra of sample A and sample B were measured at low temperatures with different excitation intensities, I_{ex} , starting from $3.7 \times 10^{-4} \text{ W/cm}^2$ up to $1.0 \times 10^4 \text{ W/cm}^2$. A comparison of the reference sample spectra with those of the DQW structure (sample B) is made in order to clarify the contribution of the second QW to the total PL output of the DQW system. Figure 2 demonstrates the low temperature, $T = 15$ K, PL spectra under different excitation intensities, I_{ex} .

Here, the spectra in each panel are normalized to the PL maximum of the PL band in sample A. The dominant PL band in each sample is assigned to the GaAsBi QW emission. At high excitation intensity a GaAs emission appears at ~ 1.510 eV as well. Common features which result from increasing the excitation power are (i) a pronounced PL maximum blue shift of the energy, (ii) growth of the integral intensity, and (iii) a change of the PL line shape. We are not able to resolve the emission from the two separate QWs in the DQW sample, however this is not surprising. After examining the structural parameters reported in Table 1 and comparing them along with their uncertainties to the results of Ref. [8], we expect the emission of the two QWs to be within the linewidth of the observed peak. And, with the observed linewidth of the single QW in sample A, we expect the two peaks in sample B to be unresolvable. Using the results of Ref. [8, 26] we can estimate the exciton transition energy for the top QW of sample B to be similar if not slightly less than that for the reference QW of sample A, and the transition energy of the bottom QW in the DQW sample to be shifted by $\approx 40\text{-}50$ meV higher than that of the QW of sample A. We emphasize that these estimates are based on highly uncertain parameters both from theory and experiment, and that the uncertainty reported in Table 1 can shift the predicted emission by at least the observed linewidth in either direction. Here, we are looking for trends, and even though we cannot resolve the spectral lines, the further line shape analysis together with theoretical calculations allows us to distinguish the individual QW contributions which are significantly important for understanding the DQW spectra behavior as I_{ex} is varied.

Figure 3 shows the changing energy of the PL maximum (E_{max}) (bottom panel), full width at half maximum (FWHM) (middle panel), and integrated PL intensity (I_{int}) (top panel) of both samples as I_{ex} is varied from 3.7×10^{-4} W/cm² to 1.0×10^4 W/cm². It is seen that E_{max} increases from 1.177 eV at the lowest intensity to 1.242 eV at the highest intensity, in sample A and from

1.192 eV to 1.240 eV in sample B over the same range of excitation intensities. However, the character of the $E_{\max}(I_{\text{ex}})$ dependences in sample B significantly differs from that observed in sample A. The PL maximum shifts very little in sample B up to $I_{\text{ex}} \approx 1.4 \text{ W/cm}^2$, whereas there is a significant shift in sample A over the same range. Remarkably, though, the dependences of the $E_{\max}$ on I_{ex} in both samples become quite similar for higher powers. The dependences of the FWHM value, Γ , on I_{ex} differ also between the two samples. Again, $\Gamma(I_{\text{ex}})$ holds a constant value ($\approx 121 \text{ meV}$) within the $I_{\text{ex}} \leq 1.4 \text{ W/cm}^2$ range in sample B whereas $\Gamma(I_{\text{ex}})$ of sample A being initially smaller, $\approx 112 \text{ meV}$ for the lowest excitation densities narrows significantly when I_{ex} grows reaching 72 meV at $I_{\text{ex}} \approx 150 \text{ W/cm}^2$. The behavior of the low temperature integrated PL intensities, I_{int} , with I_{ex} (top panel in Figure 3) is very similar in samples A and B. Following [19] we have fitted these dependences by a power law given by, $I^{\text{int}}(I_{\text{ex}}) = AI_{\text{ex}}^{\zeta}$ and found $\zeta \approx 1$ for the low power region, and $\zeta \approx 0.79$ for $I_{\text{ex}} > 0.1 \text{ W/cm}^2$. Given that the relation $I^{\text{int}}(I_{\text{ex}}) = AI_{\text{ex}}^{\zeta}$ is ascribed to the mechanisms of radiative recombination in semiconductors, we conclude that in the low power regime, the linearity indicates recombination primarily from localized excitons, whereas in the high power regime the sublinear power law indicates free exciton recombination through competing radiative and nonradiative channels [7, 8, 19].

All of the measurements above were carried out at low temperature. We note that it is possible that the local temperature can increase due to absorption of the laser light, however prior experience has shown that the cooling power of our cryostat system is sufficient to maintain low temperatures up to an excitation power regime on the order of $I_{\text{ex}} \sim 1.0 \times 10^4 \text{ W/cm}^2$. Additionally, we can see below in Figure 9 that the PL maxima red-shift at a rate of $\sim 0.5 \text{ meV/K}$ throughout the low temperature regime. In Figure 8, we see that the PL maxima are still blue-shifting up to

the highest powers. So, we conclude that heating effects are minimal. While the PL maxima and the integrated intensity do reveal a tendency for saturation at the highest intensities, we assume that the local heating is not a factor in our analysis. However, as a result we restrict our main conclusions below to excitation regimes less than, $I_{ex} \sim 1.0 \times 10^3 \text{ W/cm}^2$.

Let us now examine the PL line shape more closely under various excitation densities. Figure 4 shows the PL spectra and Gaussian fits of sample A (top panel) and B (bottom panel) measured at low temperature, $T = 15 \text{ K}$, and low excitation power, $I_{ex} = 3.7 \times 10^{-4} \text{ W/cm}^2$. The spectrum of sample A is fit well using three Gaussians. Two of them, lower by energy and shown with dash lines in Figure 4, we assign to bound excitons [7, 8, 19] localized by defects in the QW structure and caused by disorder in the bismides [17, 38, 39]. Their envelope determines the low-energy asymmetry of the PL spectrum and is assigned to the E_X^B transitions as labeled in the figure. The E_X^B band is comparatively broad ($\sim 100 \text{ meV}$), because it is composed of two bands separated by $\sim 35 \text{ meV}$. At $\sim 60 \text{ meV}$ higher in energy we find the PL band, E_X , shown in Figure 4 (top panel), which has a significantly smaller FWHM ($\sim 60 \text{ meV}$). This band is attributed to the emission of QW excitons. Typically, at low temperatures, T , and excitation intensities the PL spectra of disordered semiconductor alloys, like $\text{GaAs}_{1-x}\text{Bi}_x$, are dominated by the contribution of localized excitons which generally contribute to the long wavelength anisotropy of the PL bands, whereas the coexisting free QW excitons determine the steeper high energy side of the PL band. By changing temperature and excitation intensity it is possible to maximize the contribution of free-excitons and of band-to-band recombination, which eventually at high T will dominate the PL spectra with respect to that of the localized states [40,41,24]. It has been shown [40] that at 200 K for $\text{GaAs}_{1-x}\text{Bi}_x$ samples the PL lineshapes become

inhomogeneously and symmetrically broadened which is typical of free excitons or of band-to-band transitions in disordered alloys.

The fit of the PL spectrum of the DQW sample B we performed assuming that each quantum well possesses its own bound and free QW excitons and the distance between the maxima of the E_X^B and E_X bands for both QWs of the DQW pair is similar to the 60 meV shift found between E_X^B and E_X in the SQW. Figure 4 (bottom panel) shows the results of the best fit. The low energy asymmetric peaks we again assign to the bound excitons, $1 E_X^B$ and $2 E_X^B$, and the next higher energy peaks we attribute to the free excitons in the top QW1, $1 E_X$, and in the bottom QW2, $2 E_X$, of the DQW structure. The energies for these two QWs can be calculated using the data presented in Table 1. The influence of strain on the band structure in such highly strained QWs was taken into account using the Pikus-Bir Hamiltonian [42]. Following Ref. [22] the light-heavy hole splitting has been calculated and the Schrödinger equation for the system under consideration was reduced to:

$$-\frac{\hbar^2}{2} \frac{\partial}{\partial z} \left[\frac{1}{m^*(z)} \frac{\partial \psi_n(z)}{\partial z} \right] + V(z) \psi_n(z) = E_n \psi_n(z) \quad (1)$$

with

$$V(z) = \begin{cases} 0, & z \in (-\infty, L) \cup (L + d_{QW1}, L + d_{QW1} + d_B) \cup (L + d_{QW1} + d_B + d_{QW2}, \infty) \\ V_1, & z \in (L, L + d_{QW1}) \\ V_2, & z \in (L + d_{QW1} + d_B, L + d_{QW1} + d_B + d_{QW2}) \end{cases}. \quad (2)$$

Here E_n and ψ_n in Eq. (1) are the energy and the wave-function related to n th subband, respectively. Potential $V(z)$ in Eq. (2) includes three parameters for each QW in the DQW structure: the QW depth (V_i), the effective mass in the (100) direction (m_i^*), and the QW width (d_{QWi}), and also thickness of barrier separated two neighboring quantum wells, d_B . V_i corresponds to the band gap discontinuities ΔE_c , ΔE_v^{hh} , and ΔE_v^{lh} for electrons, heavy-, and light-holes, respectively. Structure parameters d_{QWi} and d_B are known from our HR-XRD study and the bismuth concentrations are given in Table 1. Using these concentrations and recently reported band off-sets determined from photoreflectance, polarization-resolved photovoltage spectroscopy, and theoretical analysis of dilute $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ heterostructures [22, 26, 29, 30] we can also determine the ΔE_c and ΔE_v^{hh} . Figure 5 shows the results of solution of equations (1) and (2) for DQW $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ heterostructures under consideration. Here the energy levels and modules of wave functions are presented for the QW2 with $x=0.03$ and $d_{QW2}=4.9$ nm and QW1 having $x=0.04$ and $d_{QW1}=5.0$ nm. These QWs are separated by a GaAs barrier of 6.2 nm thickness. As follows from Figure 5 for the bismuth concentration $x \leq 0.04$ and $d_{QW} \leq 5.0$ nm the conduction band of the structure has only one discrete electronic state e1 and the valence band possesses at least two heavy hole states hh1 and hh2 in each QW. Allowed optical transitions $e1 \rightarrow hh1$ are shown in Figure 5 by solid arrows, while forbidden transitions $e1 \rightarrow hh2$ are represented with dash arrows. We demonstrate in Figure 5 only the states which are involved in the PL process and the states related to the light holes are not shown. It is of importance also that as can be seen from Figure 5, the states hh1 in QW2 and hh2 in QW1 are very close by energy in the DQW structure, and the energy of $e1 \rightarrow hh1$ transition in QW2 is only slightly higher than the energy of the $e1 \rightarrow hh2$ transition in QW1. Taking into account the energy scheme of the DQW structure shown in Figure 5 let us continue the line shape analysis. It is

worth mentioning that in our model, the QWs have offsets from GaAs in both the conduction and the valence bands and are considered to form type-I heterojunctions with GaAs. The PL measurements along with $\mathbf{k-p}$ calculations also provide confirmation of type-I band offset at the $\text{GaBi}_x\text{As}_{x-1}/\text{GaAs}$ heterointerface near $x = 2\%$ [30]. Additionally, the transitions related to the excited states in the QWs are clearly observed for samples with high Bi concentration of 5.6%, confirming that these quantum wells are of type I [26]. Nevertheless there are a number of results giving evidence of type-II diluted bismides [37]. It was found that multi-QWs consisting of 3 or 3.5 pairs of nominally 8.8-nm-thick GaAs layers and 5.6-nm thick $\text{GaAs}_{0.97}\text{Bi}_{0.03}$ grown by molecular beam epitaxy reveals PL that strongly suggests that GaAsBi/GaAs has a type-II band configuration. However, recent studies of dilute bismides have demonstrated that Bi alloying can be exploited to engineer the conduction as well as the valence band of III-V semiconductors and will drive further investigations and innovative applications of the peculiar electronic properties of dilute bismides [43].

The ratios of the magnitudes of all the PL constituents derived from the PL band decomposition depends on I_{ex} and the temperature and in fact determines peculiarities of the PL line shape behavior both in the reference and in the DQW sample. At low temperatures and excitation intensities the emission caused by bound excitons is comparable to that of the QW free excitons, because the QW excitons are effectively trapped by defects. For lower I_{ex} we could even expect that the bound exciton emission could be more intense than the emission from the free excitons. As I_{ex} increases the fraction of free QW excitons in comparison to bound excitons grows, and they finally dominate the QW PL line shape at higher excitation intensities. Therefore, the observed shift of the PL maxima to higher energies in Figure 2 as well as the decreasing of the FWHM reflects the increasing contribution of the high energy, E_x , band to the

net PL spectrum of sample A. Qualitatively, such a behavior of the PL maximum and FWHM can be demonstrated by using the envelope of two Gaussians given by:

$$I_{PL} = A_1 \exp\left\{-\frac{2(E_1 - E)^2}{\sigma_1^2}\right\} + A_2 \exp\left\{-\frac{2(E_2 - E)^2}{\sigma_2^2}\right\}. \quad (3)$$

To demonstrate this we take the parameters derived from the fit for sample A, Figure 4, for E_1 and E_2 to be equal to E_X^B and E_X , and $\Gamma_{B,X} = \sqrt{2 \ln 2} \sigma_{1,2}$. If we vary only the ratio A_2/A_1 , the energy of the envelope maximum and the FWHM of spectral distribution given by Eq. (3) will evolve as shown in Figure 6a, which are very similar to those observed for $E_{\max}(I_{ex})$ and $\Gamma(I_{ex})$ in Figure 3 for the reference sample A in the region of low excitation densities. This indicates that our assignment of exciton processes in this sample for low temperature and excitation intensities is very plausible and can be applied also for the description of the DQW sample.

However, further increase of the excitation intensity leads to an increase of the FWHM which cannot be explained in the framework of the two band approximation given by Eq (3). In order to explain the non monotonic change of the PL FWHM for higher excitation densities shown in Figure 3 we must consider also the excited QW states which can evolve in the PL spectrum due to saturation of the ground exciton QW state [7, 8, 32]. Such states can be the hh2 states as shown in Figure 5. The calculated distance between hh1 and hh2 is ~ 55 meV. Figure 7, upper panel, presents the fitting results for the PL spectrum measured in sample A at high excitation density, $I_{ex}=1$ kW/cm², and low temperature. Besides the PL band, E^B , evolved from the bound exciton states, E_X^B , seen in the low-intensity PL spectra of sample A (Figure 4) we distinguish also the E_{hh1}^{el} emission related to the $e1 \rightarrow hh1$ transitions in the QW, and an additional

Gaussian E_{hh2}^{e1} related to the $e1 \rightarrow hh2$ transitions in this QW. The observed high energy tail of the PL band in sample A is then easily identified with the QW excited state, E_{hh2}^{e1} , which turns out to be ~ 52 meV higher in energy than E_{hh1}^{e1} . At this high excitation density we observe also the E_X^{GaAs} band related to the bulk GaAs. Inclusion of the $e1 \rightarrow hh2$ transitions in our consideration requires some comments. Indeed these transitions are normally parity forbidden for the symmetric square wells. Nevertheless they are predicted and observed in many cases [44-46]. So, it has been demonstrated [44] that extensive valence-band mixing can take place in the GaAs QWs. This band-mixing effect leads to manifestation of a very strong "forbidden" transition as the energy of the valence subband involved becomes close to that of another valence subband which participates in an allowed transition. It takes place in case of first light-hole and the second heavy-hole subbands in GaAs QW [44]. Such a condition is realized also in case of our structure. The calculation of the energy scheme performed using Eq. (1)-(2) gives the energy of lh1 states (not shown in Figure 4) to be close to the energy of hh2 states both in sample A and in sample B. Strong anisotropic forbidden $1e \rightarrow 2hh$ transitions comparable to the allowed transitions have been observed in a series of $In_xGa_{1-x}As/GaAs$ SQW with well width spreading over 3 nm and 7 nm at 80 K and ascribed to the coupling of heavy and light holes caused by the In segregation [46]. The quality of GaAsBi QW is also dependent on the Bi composition and the growth temperature. For particular growth condition, the flux has to be precisely controlled because a shortage of Bi can result in a surface roughness whereas a Bi excess causes formation of Bi droplet [23, 27, 37]. All these factors favor lifting the parity restrictions for the $1e \rightarrow 2hh$ transitions in our dilute bismides.

Using the results of low-intensity PL line shape analysis and involving the QW excited states we performed the high power fit of PL spectra of sample B (Figure 7, bottom panel). Exciton transitions $1E_X^B$, $1E_X$ and $2E_X^B$, $2E_X$ observed in the low-intensity regime for sample B (Figure 4, bottom panel) evolve in the $1E^B$, $1E_{hh1}^{e1}$ and $2E^B$, $2E_{hh1}^{e1}$ electron-hole transitions in case of high excitation power. Additionally the QW excited states $1E_{hh2}^{e1}$ and $2E_{hh2}^{e1}$ are distinguished as like those in sample A. Let us consider the interaction between two QWs tracing the behavior of the QW states and leaving aside the states of bound excitons. For this purpose PL spectra of DQW structure were fitted for the entire range of excitation intensities. Comparing the fitting results for low- and high-intensity regimes (Figures 4 and 7, bottom panels) we see that the ratio of magnitudes of the $1E_X$ and $2E_X$ PL bands specifically depends on the excitation intensity. Figure 6 b) shows the character of this dependence together with the dependences of the $1E_X$ and $2E_X$ maximum energies on the I_{ex} . Using Eq. 3 as a model, we see that both the $2E_X$ and $1E_X$ energies, as well as the ratio of their band magnitudes, A_2 / A_1 , do not change visibly if the excitation intensity is less than $\sim 1 \text{ W/cm}^2$. As a result the PL line shape of sample B is dominated by the QW exciton contributions. In other words, PL line shape of the DQW sample is now almost entirely defined by the QW free exciton processes. As a result the $E_{\max}$ and FWHM values are constant up to $I_{ex} \sim 1 \text{ W/cm}^2$ in sample B as seen in Figure 3.

Further increasing of the excitation intensity leads to a significant reduction in the A_2 / A_1 ratio (Figure 6b). The origin of such reduction can be explained using the results shown in Figure 5. Here the hh1 state in QW2 is very close in energy to the hh2 state in QW1. For the purpose of this argument, we will assume the hh1 state in QW2 is sufficiently above the hh2 state in QW1 that holes captured by QW2 relax and fill the ground hh1 state before they begin to tunnel into

the hh2 state of QW1. By increasing the excitation intensity hh1 saturates and through resonant tunnel transfer into hh2 of QW1, the holes relax into the ground state of QW1. . Due to the small thickness of the barrier between QW1 and QW2 , $\approx 6.2\text{nm}$, this resonant tunneling from the filled states of QW2 into the excited state of QW1 becomes very effective and subsequently prevents further increase in the emission from QW2. This saturation results in the filling of states of QW2 up to the level of hh2 in QW1 and the apparent slight shift of the $2E_x$ maximum to higher energies as can be seen in Figure 6. On the other hand the tunneling additionally pumps QW1 at the expense of carriers in QW2. As a result the top QW mainly defines the PL behavior of the DQW structure under high excitation intensities. That is what we see in Figure 6. Thus the reason for the observed transformation of the DQW structure to single QW-like under high excitation densities is the peculiarities of the DQW energy scheme and interwell coupling caused by resonant carrier transfer from QW2 to QW1. Indeed under low excitation densities both QWs in the DQW structure are populated independently. However, when the hh1 states in QW2 become filled to the excited energy level $1E_x$ of QW1, carriers from QW2 resonantly tunnel to the excited state of QW1, and rapidly relax to the exciton ground state of QW1 thus additionally populating and strengthening the emission from this state, and exhausting the PL signal from QW2. We observe here important dynamic effects caused by the presence of QW2, significantly affecting the non-equilibrium carrier distribution due to resonant tunneling in GaAs/GaAs_{1-x}Bi_x/GaAs DQW structures. It should be noted that in order to explain the excitation-power dependencies of the PL parameters, we involve tunnelling in the asymmetric DQW structures. Even though these structures are disordered to some extent such an explanation is relevant here, because it was shown that disorder-assisted tunnelling and/or thermally-assisted tunnelling can be efficient for double quantum wells, double –barrier structures, and dielectric films [47-49].

b) Temperature dependence of PL spectra.

PL spectra of samples A and B excited with $I_{ex} = 0.4 \text{ W/cm}^2$ were measured in the temperature range from 15 K to 300 K. Typical transformation of the PL line-shape is shown in Figure 8 for temperatures changing from 15 K up to 170 K in both samples. Further temperature increase makes the signal from sample A too weak for direct comparison to sample B. Subsequent comparison of the transformation is summarized in Figure 9 including a red-shift, broadening, and an evolving asymmetry which is described below. Here is plotted: the energy of PL maximum, $E_{\max}$ (bottom panel); FWHM, Γ (middle panel); and the integrated intensities, I_{int} (top panel). The energy of the PL maximum first red shifts as the temperature increases, reaches minimal values, and then moves towards higher values under further temperature increase. The FWHM, Γ , remains nearly constant for temperatures up to $T \sim 100 \text{ K}$. Then, it increases sharply reaching a maximum at $T \sim 190 \text{ K}$ in sample A, and at $T \sim 240 \text{ K}$ in sample B. Finally, it decreases again for both samples as T approaches room temperature. This observed behavior of the PL peak position and FWHM can be explained in terms of different temperature behaviors of the PL constituents (Figures 4, 7) revealed in all measured spectra of sample A and sample B, i.e. a broad PL emission, E_X^B , of bound excitons, the significantly narrower ground state exciton emissions going from QW1, $1E_X$, and QW2, $2E_X$, and excited state emissions $1E_{hh2}^{e1}$ and $2E_{hh2}^{e1}$, respectively from QW1 and QW2. Typically the QW exciton emission rapidly quenches as the temperature increases. This leads to a domination of the bound states, E^B , in the high temperature PL spectra of GaAs/GaAs_{1-x}Bi_x/GaAs SQW. The E^B and E_{hh1}^{e1} constituents form the PL signal in sample A at high temperature, thus the PL line shape will be determined by their ratio. Following a similar analysis as above using Eq. (3) we expect that the PL maximum will

shift towards lower energies, i.e., towards the energy of the E^B band maximum, and the linewidth will be substantially increased. This is exactly what we see in Figure 9 up to ~ 170 K in sample A and ~ 220 K in sample B. Above these characteristic temperatures we observe a substantial blue shift of the PL maxima in both samples. The origin of such temperature behavior of $E_{\max}(T)$ dependence is clear from Figure 7. At high temperatures additional contributions to the PL band develop on the high energy side which arise from the thermally excited $1E_{hh2}^{e1}$ and $2E_{hh2}^{e1}$ states. This results in both the blue-shift and the narrowing seen in Figure 9. While the PL band strongly depends on the strength of the E^B , E_X , and E_{hh2}^{e1} emissions, different functional dependences of the PL emission can be realized in diluted bismides by changing temperature T and excitation intensity I_{ex} .

Finally, let us consider the origin of the much more stable PL in the DQW as compared to the SQW. This is seen in the temperature dependences of integrated PL shown in Figure 9 (top panel). We assume that the presence of the additional QW in the DQW structure influences the recombination processes in the GaAsBi QW. In general, the temperature behavior of the DQW PL resembles closely that observed in a single GaAs/GaAsBi/GaAs QW with symmetric AlGaAs cladding reported in Ref. [20]. It has been demonstrated there that introduction of symmetric AlGaAs cladding for the GaAs/GaAsBi/GaAs QW prevented the carriers from escaping the QW area into the GaAs barrier where they could recombine non-radiatively. In the description developed in Ref. [20] rate equations were considered for the intra-well relaxation along with a set of continuity equations for the density of excitons in the bulk, in the quantum wells, and Fick's law for the particle current density [50]. This approach is applied for the DQW structure also if the inter-well tunnel coupling is included. The presence of the additional QW influences the carrier distribution both in the GaAs barrier and in the GaAsBi QW because this QW serves

as an efficient trap for carriers which are thermally emitted into the GaAs barrier by the neighboring QW. As a result, thermally excited carriers stay in the active QW area. If the two QWs involved in the double QW structure were identical as one could suggest due to the absence of separate signals from each, it is difficult to understand, how the carrier redistribution between the two nearly similar QWs can help to increase activation energy of the carriers in the overall QW system. Having in mind that the growth technology of such structures is currently far from being ideal, one can also suggest that there is some other technologically uncontrolled factor that is responsible for higher room-temperature efficiency of the double-QW structure, like e.g. lower density of defects causing nonradiative losses. However, taking into account that the growth conditions for the SQW and the DQW structures were held identical this origin of higher temperature stability of DQW PL is unlikely. A more plausible explanation of the observed integrated PL stability originates from our data on the power dependence of the PL intensity in the DQW structure described in subsection a). According to these data our DQW structure has to be considered as an asymmetric coupled double QW system with tunnelling between hole states. It is well known that the tunnelling rate in QWs can be drastically increased under resonant conditions [51]. Therefore, if the temperature increases, the thermal energy partly compensates the difference between the band of the hh1 states in QW2 and the band of the hh2 states in QW1. Thus the resonant tunnelling from the filled states of the bottom QW into the excited state of the top QW becomes very effective serving as an enhanced carrier injection which partly compensates the carrier loss due to thermal escape or thermal-activated nonradiative recombination. This tunnelling becomes the origin of the observed PL stabilization in coupled asymmetric DQWs. Similar arguments have been used to explain anomalous tunnelling in photoluminescence of asymmetric coupled double InGaN/GaN quantum wells [52].

IV. Conclusions

Concluding, we have studied the structural and optical properties of a $\text{GaAs}_{1-x}\text{Bi}_x$ DQW and compared them with those of a $\text{GaAs}_{1-x}\text{Bi}_x$ SQW. It is shown that a $\text{GaAs}_{1-x}\text{Bi}_x/\text{GaAs}$ DQW possesses significantly improved optical properties as compared with the SQW system of the similar Bi composition in that an efficient photoluminescence is significantly more thermally stable in the DQW structure. The dependence of the PL on temperature and excitation intensity is well described in terms of carrier dynamics including QW ground states, bound excitons and QW excited states. An efficient tunnel coupling of quantum wells significantly influences the carrier distribution in the DQW structure under intense optical and/or thermal excitation. Strongly nonmonotonic dependences of the PL band parameters are observed under increasing excitation intensity and temperature and interpreted in terms of the competition of bound and free QW carrier contributions. Understanding of these processes in dilute $\text{GaAs}_{1-x}\text{Bi}_x$ QW structures is very important for the creation of highly efficient devices with reduced loss.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The work presented here was carried out in collaboration between all authors.

YIM, GGT, MEW, GEM and GJS defined the research theme, discussed and interpreted results of experiments, and drafted the manuscript. DF, SQY grow the samples, MS carried out XRD measurements and corresponding simulations, VGD, LD, performed spectroscopy experiments and evaluated spectra. ZYZ and SSK helped GGT to make calculations. All authors read and approved the final manuscript.

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Table 1. Experimental results for the Bi content, x , and thicknesses, d_{QW} , of the GaAsBi QWs in samples A and B as determined by HR-XRD

Sample		x (%) HR-XRD	d_{QW} (nm) HR-XRD
A		4.2 ± 0.2	3.9 ± 0.5
B	top:	4.0 ± 0.5	5.0 ± 0.5
	bot.:	3.0 ± 0.5	4.9 ± 0.6

Figure captions

Figure 1. Experimental HR-XRD rocking curves (symbols) around the GaAs (004) symmetrical Bragg reflection for samples A and B plotted together with corresponding simulations (solid lines).

Figure 2. Low temperature ($T = 15$ K) PL spectra measured at different excitation intensities in reference sample A (black line) and GaAsBi DQW sample B (red line). All spectra are normalized to PL maximum in sample A

Figure 3. Dependence of PL band parameters on excitation intensity for sample A (black squares) and sample B (red circles). The panels are: (bottom) energy of the PL maximum (E_{max}), (middle) FWHM, and (top) integrated PL intensity (I_{int}) measured under I_{ex} varying from 3.7×10^{-4} W/cm² up to 1.0×10^4 W/cm².

Figure 4. PL spectra of sample A (top panel) and B (bottom panel) measured at low temperature, $T = 15$ K, and low excitation power, $I_{ex} = 3.7 \times 10^{-4}$ W/cm². Fit of the PL bands related to bound excitons is shown with dash lines whereas their envelope E_x^B is asymmetric solid line.

Figure 5. Energy levels (red lines) and modules of the wavefunctions calculated from Eqs (1), (2) for the double quantum well structure GaAs_{1-x}Bi_x/GaAs with structural parameters taken from Table 1. Allowed optical transitions are shown by solid arrows, forbidden transitions are given with dash arrows.

Figure 6. a) Change of the energy of the envelope maximum (left ordinate) and the FWHM (right ordinate) of the spectral distribution given by Eq. (3) as the ratio A_2 / A_1 varies. b) The change of the $1E_x$ and $2E_x$ energies, and the ratio of PL magnitudes A_2 / A_1 versus the I_{ex} in sample B.

Figure 7. PL spectra of sample A (top panel) and B (bottom panel) measured at low temperature, $T = 15$ K, and high excitation power, $I_{ex} = 1000$ W/cm². Fit of the PL spectra is performed using bound states E^B , QW ground states E_{hh1}^{e1} , and QW excited states E_{hh2}^{e1} for each GaAs_{1-x}Bi_x QW.

Figure 8. PL spectra of samples A (red curve) and B (black curve) excited with $I_{ex} = 0.4$ W/cm² and measured at different temperatures.

Figure 9. Temperature induced changes of PL band: the energy of PL maximum, E_{max} , (bottom panel), FWHM, Γ , (middle panel), and integrated intensities, I_{int} , (top panel) in samples A (black squares) and B (red circles). $I_{ex} = 0.4$ W/cm².

Figures

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 6

Figure 7

Figure 8

Figure 9