Enhanced Absorption by Linewidth Narrowing in Optically Excited Type-II Semiconductor Heterostructures

M. Stein,* C. Lammers, M. J. Drexler, C. Fuchs, W. Stolz, and M. Koch
Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

(Received 14 March 2018; published 2 July 2018)

We experimentally report a surprising linewidth narrowing of the direct exitonic 1 *s* heavy-hole transition in a type-II quantum well system. This narrowing, which builds up on a pico- to nanosecond timescale, causes a transient enhanced absorption at the spectral peak position of the excitonic resonance. We discuss how this effect depends on experimental parameters such as excitation density, temperature, and barrier width. We cannot attribute this effect to known physical mechanisms.

DOI: 10.1103/PhysRevLett.121.017401

Quantum well (QW) based semiconductor heterostructures are ideal model systems to study the properties of low-dimensional carrier systems. Recently, so called type-II structures, which were studied intensively in the late 1980s and early 1990s [1–9], gained attention again as prototypical structures for charge-transfer states [10–15]. They can serve as well-defined high quality model systems to study, e.g., the impact of the interface morphology on charge-transfer processes, which are of importance for nearly all electronic and optoelectronic devices [16]. Type-II semiconductor heterostructures contain two adjacent but different QWs, often with a barrier between them. The energy levels in the conduction and valence band are designed such that for a particular photon energy only one QW is excited and that subsequently either electrons or holes find energetically more favorable states in the other QW and undergo a spatial charge transfer. One powerful experimental method to gain insights into their physics is ultrafast optical pump-probe spectroscopy [1,6,17]. After optical excitation excitonic lines can exhibit reduced absorption, shifts, and broadening [2–4,17]. These signatures are associated with optical nonlinearities arising from the many-particle nature of the system [18–20]. These are phase-space filling, band gap renormalization, screening and excitation induced dephasing.

In this Letter we report an induced absorption of the excitonic resonance due to a linewidth narrowing. The effect, which arises several ten to hundred picoseconds after optical excitation, is observed at the direct type-I 1 *s* heavy-hole (hh) resonance in a type-II QW structure.

We study a set of three different type-I and type-II QW structures, consisting of 5 periods of $Ga_{1-x}In_xAs/GaAs/GaN_yAs_{1-y}$ layers with a cap layer of 45 nm GaAs and a buffer layer of 250 nm GaAs grown on GaAs substrate. The thickness of the intermediate GaAs barrier is $d_{GaAs} = 1.5$ nm (samples *A* and *B*) and $d_{GaAs} = 6.0$ nm (sample *C*) as confirmed by TEM and XRD measurements. Further structural parameters such as the nitrogen concentration (N_N) are listed in Table I. Linear absorption is measured using a tungsten light source focused to a 60 μm large spot and an optical spectrum analyzer. The carrier dynamics are studied using optical pump-white light probe spectroscopy. The setup is operated by a titan-sapphire laser based regenerative amplifier system, which delivers laser pulses with an energy of 5 mJ and a temporal duration of 35 fs with a repetition rate of 1 kHz. Central photon energies can be tuned via an optical parametric amplifier. A small fraction of the amplifier output experiences a variable delay before being focused onto a sapphire crystal in order to generate white-light supercontinuum probe pulses. The spectra of the transmitted white light are recorded by a spectrometer which contains a liquid nitrogen cooled (GaIn)As line detector and has a spectral resolution of 1 nm. The experiments shown are performed at 10 K in a liquid helium cryostat.

The linear absorption spectra of sample *B* and sample *C*, both with a type-II band alignment, are shown in Fig. 1 as solid lines. A schematic band diagram of these samples and the corresponding wave functions are given in the inset of Fig. 1. The minimum energy level of the conduction band is found in the Ga(NAs) QWs while the valence band maximum is in the (GaIn)As layers. Because of the small valence band offset of the Ga(NAs) QWs [21], confined hole states are expected only in the (GaIn)As QWs. Since the indium content and the well width are nearly the same for both samples, both spectra show an absorption peak

TABLE I. Structural parameters from TEM and HR-XRD studies for the set of type-I and type-II QW systems.

Sample	d_{GaAs} (nm)	N_{In} (%)	N_N (%)	$d_{(GaIn)As}$ (nm)	$d_{Ga(NAs)}$ (nm)	Band alignment
A	1.5	24.0	0.6	10.0	7.4	Type-I
B	1.5	23.5	4.8	10.3	4.5	Type-II
C	6.0	23.6	5.0	10.5	4.6	Type-II

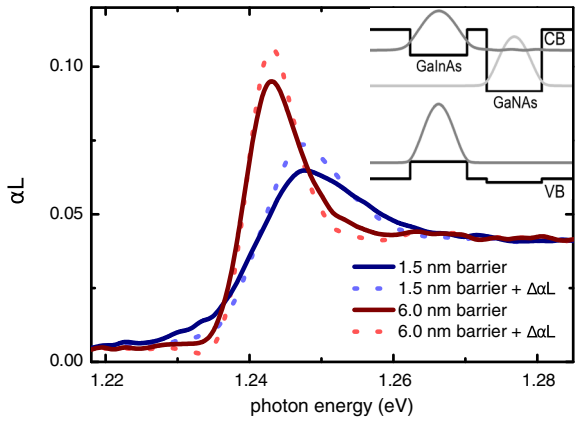

FIG. 1. Solid lines: Linear absorption spectra of the QW samples with a type-II band alignment and 1.5 nm (blue, sample *B*) and 6.0 nm (red, sample *C*) thick barriers, respectively. Dashed lines: Sum of the linear absorption and its respective differential absorption for a pump-probe delay of 5 ns. The inset is a schematic of the band diagram together with the corresponding wave functions.

around 1.245 eV. This absorption peak, which results from the 1 *s* hh exciton in the (GaIn)As QWs, is noticeably slimmer and more pronounced for sample *C* with a 6.0 nm thick barrier. In this case the transition is mainly inhomogeneously broadened and best described by a Gaussian function with a full width at half maximum (FWHM) of 8.3 meV. (See Supplemental Material [22] for details of the fit functions.) In the case of sample *B* the same absorption peak experiences an additional homogeneous broadening which results from the fast electron transfer from the (GaIn)As QWs to the Ga(NAs) QWs. Therefore, the line shape of the 1 *s* exciton transition of sample *B* is best reproduced by a convolution of a Gaussian and a Lorentzian, thus a Voigt profile. Here, the Lorentzian part of the best fit has a broadening of 6.0 meV which corresponds to a dephasing time of 220 fs. The broadening of the Gaussian part is 12.4 meV which results in a FWHM of ∼15.9 meV. To analyze the charge carrier dynamics, we perform optical pump-optical probe (OPOP) measurements under cross-linear-polarized excitation. The excitation spectrum is centered at 1.34 eV. This energy excites charge carriers in the (GaIn)As QWs but above its excitonic 1 *s* hh resonance. In Fig. 2 a contour plot of the OPOP measurements is shown for sample *B* with a type-II band alignment (right panel). For comparison, we also plot the OPOP data obtained from the type-I structure (sample *A*) in the left panel. For both samples we observe a negative differential absorption ($\Delta\alpha L$) directly after optical excitation which arises from phase-space filling. For the type-II heterostructure a fast initial recovery is observed within the first picosecond after excitation which is caused by the transfer of electrons through the barrier into the Ga(NAs) QWs [1,28]. An exponential fit to the transient (see inset of Fig. 3) yields a transfer time of 300 fs, which is in good agreement with the dephasing time of 220 fs we received from the linewidth analysis. Once this initial electron transfer is completed in sample *B*, we observe a second minimum in the $\Delta\alpha L$ signal around 40 ps as the initially hot carrier distribution cools down [28–30]. Cooling of the excited charge carriers also leads to a minimum in the reference sample at ∼75 ps. The faster cooling dynamics in the type-II sample are attributed to the fact that only holes remain in the (GaIn)As QWs [31–33]. Afterwards, the negative $\Delta\alpha L$ signature recovers for both samples on a timescale of hundreds of picoseconds due to recombination

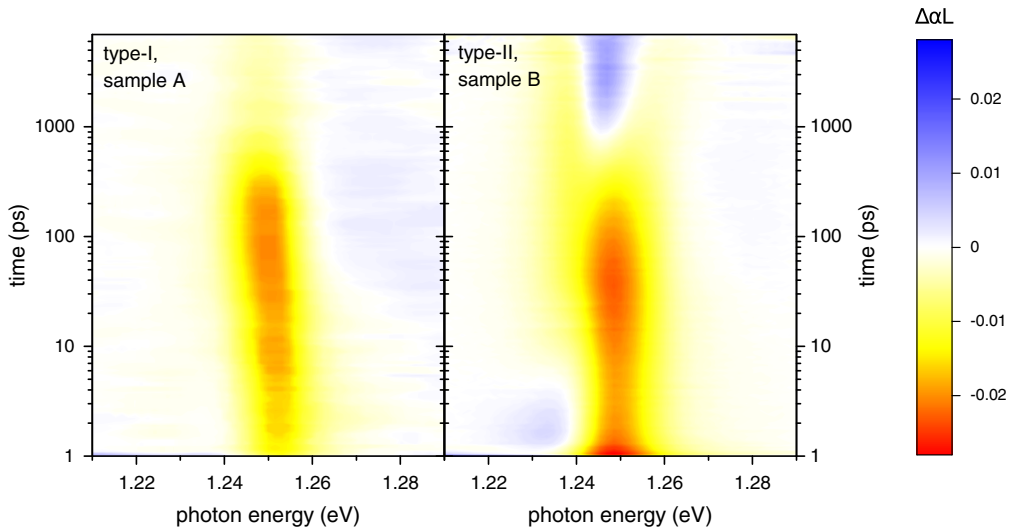

FIG. 2. Left panel: Contour plot of the optical pump-optical probe spectra for the reference sample *A* with a type-I band alignment. Right panel: Contour plot for sample *B* with a type-II band alignment and a 1.5 nm thick GaAs barrier. The plot illustrates the changes of the absorption ($\Delta\alpha L$) after an optical excitation for time delays ranging from femtoseconds to several nanoseconds. In order to plot a logarithmic time scale the optical excitation is set to 1 ps.

processes of the excited charge carriers and/or the population of trap states.

The remarkable feature reported here is a local peak in the differential absorption of sample B. It occurs after 1 ns and is energetically positioned at the 1 s hh transition. This peak reaches its maximum ~3 ns after excitation and sustains at this level for the next 4 ns. The positive $\Delta\alpha L$ signature is surrounded by a negative differential absorption which is a typical signature of a linewidth narrowing. Such an induced absorption is absent in the type-I sample. The formation of this positive $\Delta\alpha L$ signature out of a pure bleaching signature is further highlighted in Fig. 3 where we plot the $\Delta\alpha L$ spectra for a series of discrete time delays. For a time delay of 200 ps we observe a broad negative signal arising from phase-space filling. With progressing time a local maximum arises within this bleaching signal at 1.244 eV which is already very noticeable at 500 ps. As this local maximum evolves into a prominent peak in the $\Delta\alpha L$ spectrum on a nanosecond timescale it shifts to 1.247 eV, which is close to the central position of the bleaching signature at 1.248 eV. For a time delay above 1 ns the absorption is enhanced at this peak while it is decreased above and below this local maximum. A spectral integration over the whole region from 1.215 to 1.28 eV gives an integrated $\Delta\alpha L$ signal close to zero (see the inset of Fig. 3). Since the integrated signature is zero for late times, the oscillator strength of the excitonic 1 s hh transition is not increased. Hence, we conclude that the locally enhanced absorption is caused by a linewidth narrowing. However, such a signature of a linewidth narrowing is not observed for type-I heterostructures, neither in our type-I reference nor in the literature. Here, the negative $\Delta\alpha L$ signature just disappears on a nanosecond timescale which is a typical recombination time for type-I QW samples.

We now discuss how the observed linewidth narrowing depends on experimental parameters. First, we investigate how the buildup of the linewidth narrowing depends on the carrier density. Figure 4 shows the evolution of the $\Delta\alpha L$ signal for three different excitation densities. Here we observe that the positive $\Delta\alpha L$ arises later for an increased carrier density. Nevertheless, the amplitude of the signature increases with excitation density. It reaches a value of 0.01 at late times for a photon density of 6.6×10^{14} photons/cm^2. This corresponds to more than 10% of the excitonic absorption at its peak value.

To investigate the influence of the sample temperature on the observed feature we have performed additional experiments for 40, 120, and 200 K (the results of this experiments are shown in the Supplemental Material [22]). We observe a positive $\Delta\alpha L$ signal for all temperatures. Thus, we can exclude that the formation of quasiparticles like charge-transfer excitons is responsible for the observed signature. Moreover, we find that the signature of an enhanced absorption builds up faster with increasing temperature.

The experiments shown so far are carried out with a photon energy of 1.34 eV which, at 10 K, corresponds to an excess energy of 90 meV. To investigate the impact of the optical excitation energy we also performed experiments with a photon energy of 1.25 eV, which is resonant to the 1 s hh transition. For comparable charge carrier densities we find that the positive $\Delta\alpha L$ signal evolves at the same time (see Supplemental Material [22]). We therefore conclude that the excitation energy is not a decisive parameter for the observations presented here.

Finally, we focus on structural sample parameters. The most important parameter is the intermediate GaAs barrier

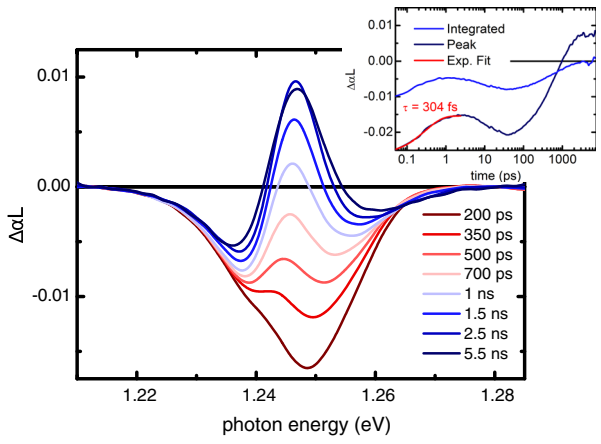

FIG. 3. Differential absorption spectra of sample B for different time delays. The inset shows transients at 1.248 eV (peak) as well as integrated over the whole bleaching signature from 1.215 to 1.28 eV (integrated).

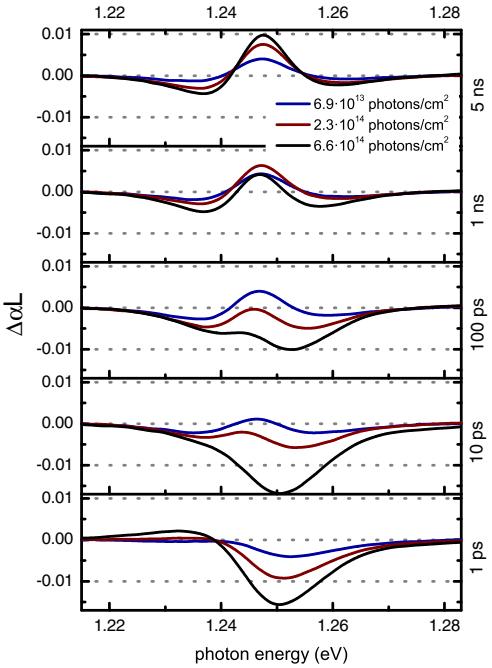

FIG. 4. Differential absorption spectra of sample B for three different excitation densities.

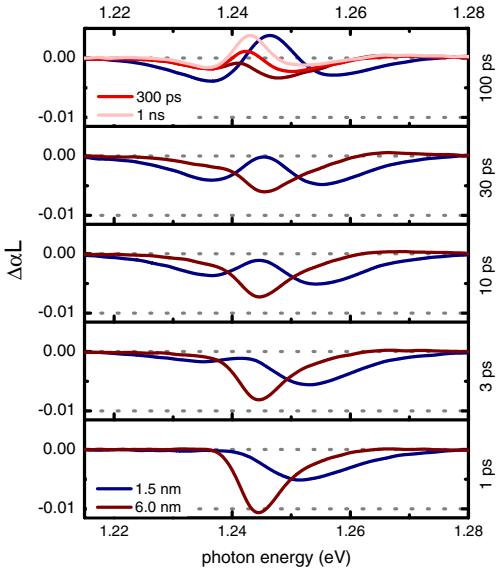

FIG. 5. Comparison of the differential absorption spectra of both samples with a type-II band alignment, i.e., sample B with a barrier width of 1.5 nm and sample C with a barrier width of 6.0 nm.

width as it largely determines the transfer and recombination dynamics in the sample [5]. For a thicker barrier the transfer time as well as the recombination lifetime are enhanced. Figure 5 shows a comparison between sample B and sample C with barrier widths of 1.5 and 6.0 nm, respectively. The experiments have been performed with comparable excitation densities of 1.1×10^{14} photons/cm^2 for sample B and 6.3×10^{13} photons/cm^2 for sample C. A locally enhanced absorption is observed for both samples. Yet, the occurrence of this signature is delayed for sample C in comparison to sample B. This is not surprising as charge transfer and recombination are slower for the thick barrier sample. However, it is surprising that a positive $\Delta\alpha L$ signature occurs several hundred picoseconds later in sample C even though the charge transfer itself happens within tens of picoseconds as OPOP transients reveal.

The above data clearly demonstrate a reduction of the excitonic linewidth after optical excitation in type-II heterostructures. At present we have no microscopic explanation for this surprising effect. The spectral width of excitonic lines results from homogeneous and inhomogeneous broadening. The latter arises from structural inhomogeneities such as compositional disorder or well width fluctuations. The homogeneous linewidth is associated with the coherent lifetime of an optically excited state via $\Gamma_{\mathrm{hom}} = (2\hbar/T_2)$, where Γ_{hom} is the homogeneous linewidth and T_2 is the so-called dephasing time. In a type-I structure the dephasing time is determined by carrier-phonon and carrier-carrier scattering. For low excitation densities and at low temperatures one typically finds dephasing times of a few picoseconds for excitonic hh transitions [34–36]. In a type-II structure the spatial transfer of charge carriers also destroys the coherence. For our sample with a 1.5 nm barrier we determine a transfer time of 300 fs corresponding to an homogeneous linewidth of 4.3 meV by OPOP spectroscopy and an homogeneous linewidth of 6.0 meV corresponding to a dephasing time of 220 fs by a line shape analysis of the linear absorption spectrum. Therefore, we conclude that the fast transfer of charge carriers is mainly responsible for the destruction of the coherence in this sample. If for some unknown reason the dephasing time of the weakly excited sample would increase to roughly 1 ps this could explain the observed linewidth narrowing of ~2.9 meV. This implies that the transfer time would have to increase from 300 fs to above 1 ps. Yet, we observe a linewidth narrowing for sample C as well. Here, the linewidth is reduced by 0.9 meV. However, the main absorption peak of sample C can only be described by an inhomogeneous broadening and already features a transfer time in the ps range so that a further increase will not affect its linewidth. Since it is very unlikely that the surprising effect of a linewidth narrowing is caused by two different mechanisms in both samples, we exclude that it arises from an altered transfer time in the excited sample.

It is well known that electric fields in the growth direction lead to a broadening of the excitonic linewidth [37,38]. Hence, it is conceivable that the unexcited QW structure is slightly tilted, e.g., as a consequence of unwanted background doping. If this initial field is compensated by the charge carrier concentration in the two neighboring QWs the excitonic resonances could be narrowed since the structure would be untilted. Yet, the field induced linewidth broadening is always associated with a spectral shift [37]. As we do not observe any spectral shifts for the densities investigated (see Fig. 4), we exclude that field-induced effects are responsible for the linewidth narrowing. In addition, field-induced effects would directly couple to the transfer of charge carriers through the barrier. However, such a direct coupling of the linewidth narrowing to the charge transfer is not observed. While the charge transfer takes place on a picosecond to subpicosecond timescale, it takes several hundred picoseconds until the linewidth narrowing occurs.

Hence, we cannot attribute our experimental observations to any known physical mechanisms. We hope that the experimental observations reported here will stimulate theoretical investigations in the future.

In conclusion, we observe the astonishing buildup of an enhanced absorption due to a linewidth narrowing at low carrier densities in type-II QW heterostructures. In particular this means that the excitonic resonance in the linear absorption is spectrally sharper in the excited sample than in the unexcited sample. Such a signature does not occur in a type-I reference sample. It takes several tens to hundreds of picoseconds for the enhanced absorption to develop and it can reach up to 10% of the linear absorption of the

samples investigated. The reported signature arises faster for lower carrier densities, higher sample temperatures, and for samples with a lower intermediate barrier thickness. Since type-II semiconductor heterostructures are prototypical structures for a vast number of systems with charge-transfer states, we believe that our findings will stimulate similar investigations on other charge-transfer systems, such as donor-acceptor systems or heterojunction solar cells, where the spatial charge transfer through an interface is essential for their operation.

This work is a project of the Collaborative Research Center SFB 1083 funded by the Deutsche Forschungsgemeinschaft.

*markus.stein@physik.uni-marburg.de

[1] J. Feldmann, R. Sattmann, E. O. Göbel, J. Kuhl, J. Hebling, K. Ploog, R. Muralidharan, P. Dawson, and C. T. Foxon, Phys. Rev. Lett. **62**, 1892 (1989).

[2] G. R. Olbright, W. S. Fu, A. Owyoung, J. F. Klem, R. Binder, I. Galbraith, and S. W. Koch, Phys. Rev. Lett. **66**, 1358 (1991).

[3] G. R. Olbright, W. S. Fu, J. F. Klem, H. M. Gibbs, G. Khitrova, R. Pon, B. Fluegel, K. Meissner, N. Peyghambarian, R. Binder, I. Galbraith, and S. W. Koch, Phys. Rev. B **44**, 3043 (1991).

[4] K. Meissner, B. Fluegel, R. Binder, S. W. Koch, G. Khitrova, and N. Peygambarian, Appl. Phys. Lett. **59**, 259 (1991).

[5] I. Galbraith, P. Dawson, and C. T. Foxon, Phys. Rev. B **45**, 13499 (1992).

[6] J. Feldmann, J. Nunnenkamp, G. Peter, E. Göbel, J. Kuhl, K. Ploog, P. Dawson, and C. T. Foxon, Phys. Rev. B **42**, 5809 (1990).

[7] I. H. Libon, S. Baumgärtner, M. Hempel, N. E. Hecker, J. Feldmann, M. Koch, and P. Dawson, Appl. Phys. Lett. **76**, 2821 (2000).

[8] R. Binder, I. Galbraith, and S. W. Koch, Phys. Rev. B **44**, 3031 (1991).

[9] L. V. Butov, A. Zrenner, G. Abstreiter, G. Böhm, and G. Weimann, Phys. Rev. Lett. **73**, 304 (1994).

[10] D. Snoke, S. Denev, Y. Liu, L. Pfeiffer, and K. West, Nature (London) **418**, 754 (2002).

[11] O. Vänskä, I. Tittonen, S. W. Koch, and M. Kira, Phys. Rev. Lett. **114**, 116802 (2015).

[12] C. Berger, C. Möller, P. Hens, C. Fuchs, W. Stolz, S. W. Koch, A. R. Perez, J. Hader, and J. V. Moloney, AIP Adv. **5**, 047105 (2015).

[13] C. Möller, C. Fuchs, C. Berger, A. R. Perez, M. Koch, J. Hader, J. V. Moloney, S. W. Koch, and W. Stolz, Appl. Phys. Lett. **108**, 071102 (2016).

[14] C. Lammers, M. Stein, C. Berger, C. Möller, C. Fuchs, A. R. Perez, A. Rahimi-Iman, J. Hader, J. V. Moloney, W. Stolz, S. W. Koch, and M. Koch, Appl. Phys. Lett. **109**, 232107 (2016).

[15] M. Stein, C. Lammers, P.-H. Richter, C. Fuchs, W. Stolz, M. Koch, O. Vänskä, M. J. Weseloh, M. Kira, and S. W. Koch, Phys. Rev. B **97**, 125306 (2018).

[16] H. Kroemer, Rev. Mod. Phys. **73**, 783 (2001).

[17] A. Alexandrou, M. K. Jackson, D. Hulin, N. Magnea, H. Mariette, and Y. M. d'Aubigné, Phys. Rev. B **50**, 2727 (1994).

[18] M. Kira and S. Koch, Prog. Quantum Electron. **30**, 155 (2006).

[19] H. Haug and S. W. Koch, Excitonic optical stark effect, *Quantum Theory of the Optical and Electronic Properties of Semiconductors*, 5th ed. (World Scientific, Singapore, 2009), pp. 235–267.

[20] J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures*, Springer Series in Solid-State Sciences (Springer, New York, 1999).

[21] I. Vurgaftman and J. R. Meyer, J. Appl. Phys. **94**, 3675 (2003).

[22] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.121.017401, which includes Refs. [8,23–27], for details of the fit functions used for the linewidth analysis and additional experimental data.

[23] R. Steel and J. Torrie, *Principles and Procedures of Statistics: With Special Reference to the Biological Sciences* (McGraw-Hill, New York, 1960).

[24] J. Olivero and R. Longbothum, J. Quant. Spectrosc. Radiat. Transfer **17**, 233 (1977).

[25] S. D. Baranovskii, R. Eichmann, and P. Thomas, Phys. Rev. B **58**, 13081 (1998).

[26] O. Rubel, M. Galluppi, S. Baranovskii, K. Volz, L. Geelhaar, H. Riechert, P. Thomas, and W. Stolz, J. Appl. Phys. **98**, 063518 (2005).

[27] O. Rubel, S. D. Baranovskii, K. Hantke, B. Kunert, W. W. Rühle, P. Thomas, K. Volz, and W. Stolz, Phys. Rev. B **73**, 233201 (2006).

[28] K. Meissner, B. Fluegel, R. Binder, S. W. Koch, G. Khitrova, and N. Peygambarian, Appl. Phys. Lett. **59**, 259 (1991).

[29] C. V. Shank, R. L. Fork, R. F. Leheny, and J. Shah, Phys. Rev. Lett. **42**, 112 (1979).

[30] H. Roskos, B. Rieck, A. Seilmeier, and W. Kaiser, Appl. Phys. Lett. **53**, 2406 (1988).

[31] J. Shah, A. Pinczuk, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **54**, 2045 (1985).

[32] H. J. Polland, W. W. Rühle, J. Kuhl, K. Ploog, K. Fujiwara, and T. Nakayama, Phys. Rev. B **35**, 8273 (1987).

[33] R. A. Höpfel, J. Shah, and A. C. Gossard, Phys. Rev. Lett. **56**, 765 (1986).

[34] R. Hellmann, M. Koch, J. Feldmann, S. T. Cundiff, E. O. Göbel, D. R. Yakovlev, A. Waag, and G. Landwehr, Phys. Rev. B **48**, 2847 (1993).

[35] L. Schultheis, A. Honold, J. Kuhl, K. Köhler, and C. W. Tu, Phys. Rev. B **34**, 9027 (1986).

[36] M. Koch, G. von Plessen, J. Feldmann, and E. O. Göbel, Chem. Phys. **210**, 367 (1996), confined Excitations in Molecular and Semiconductor Nanostructures.

[37] D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. H. Wood, and C. A. Burrus, Phys. Rev. B **32**, 1043 (1985).

[38] C. F. Klingshirn, *Semiconductor Optics* (Springer Science & Business Media, New York, 2012).