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Blueshifts of the emission energy in type-II quantum dot and quantum ring nanostructures

P. D. Hodgson,^{1,a)} R. J. Young,¹ M. Ahmad Kamarudin,^{1,2} P. J. Carrington,¹ A. Krier,¹ Q. D. Zhuang,¹ E. P. Smakman,³ P. M. Koenraad,³ and M. Hayne¹

¹Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom

²Department of Physics, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

³Department of Applied Physics, Eindhoven University of Technology, 5612 AZ, The Netherlands

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We have studied the ensemble photoluminescence (PL) of 11 GaSb/GaAs quantum dot/ring (QD/QR) samples over ≥ 5 orders of magnitude of laser power. All samples exhibit a blueshift of PL energy, ΔE , with increasing excitation power, as expected for type-II structures. It is often assumed that this blueshift is due to band-bending at the type-II interface. However, for a sample where charge-state sub-peaks are observed within the PL emission, it is unequivocally shown that the blueshift due to capacitive charging is an order of magnitude larger than the band bending contribution. Moreover, the size of the blueshift and its linear dependence on occupancy predicted by a simple capacitive model are faithfully replicated in the data. In contrast, when QD/QR emission intensity, I , is used to infer QD/QR occupancy, n , via the bimolecular recombination approximation ($I \propto n^2$), exponents, x , in $\Delta E \propto I^x$ are consistently lower than expected, and strongly sample dependent. We conclude that the exponent x cannot be used to differentiate between capacitive charging and band bending as the origin of the blueshift in type-II QD/QRs, because the bimolecular recombination is not applicable to type-II QD/QRs. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818834>]

I. INTRODUCTION

There are many potential applications for self-assembled quantum dots (QDs) and quantum rings (QRs), including lasers,¹ solar cells,² and quantum information processing.³ III-V heterojunctions in general provide much potential for device structures, but the reduced dimensionality (D) of QD/QRs can offer particular advantages over bulk and 2D quantum well (QW) structures; for example, lower threshold currents and higher thermal stability in lasers,⁴ and insensitivity to edge states in solar cells.⁵

The staggered type-II band alignment of GaSb/GaAs heterostructures [e.g., QW, QD, or QR] leads to spatial separation of carrier species [Fig. 1(a)] and a reduced recombination rate. Whilst this property can hinder their use in light emitting applications, it does open the possibility of use in memory devices.^{6,7} QD/QR structures with negligible charging barriers (fast write time)⁸ and large confinement energies (long storage time)^{9,10} have been demonstrated. In solar cells, the type-II QD/QR structure also provides the opportunity for efficient carrier separation and absorption of photons with energy below the band gap of the host semiconductor, improving long-wavelength response.^{11,12}

Blueshifts of emission energy as a function of increasing excitation power are not routinely seen in type-I systems, but have been observed and attributed to donor-acceptor pair recombination,¹³ composition modulation,¹⁴ or state filling.¹⁵ Type-II structures, however, have a characteristically strong blueshift with excitation power, which can affect device operation. For example, laser devices which contain

GaSb/GaAs QDs have shown significant blueshifts with injection current.¹⁶ As this blueshift is a fundamental property of type-II nanostructures, a better understanding of the underlying physics will aid in the development of devices. In the literature, it is common practice to plot PL energy versus $P^{1/3}$ to demonstrate type-II behaviour.^{17–20} Implicit in

FIG. 1. (a) Schematic band-gap diagram of a GaSb/GaAs heterostructure, including band bending. z is the growth direction. (b) Scanning tunnelling microscope image of a quantum ring cross-section; brighter regions indicate high Sb content.

^{a)}Electronic mail: p.hodgson1@lancaster.ac.uk

this are assumptions whose validity have not been properly considered. The first is that the blueshift is caused by band bending (BB). The second is that the incident laser power, P (or sometimes the recombination intensity, I), is proportional to the square of the carrier density (QD/QR occupancy), i.e., recombination is bimolecular. Here, we report the results of photoluminescence (PL) measurements of 11 GaSb/GaAs QD/QR samples, at excitation powers ranging over 5–6 orders of magnitude. We show that the dominant mechanism responsible for the excitation-power-induced blueshift is charging, not band bending. This should result in the exponent, x , in the power law I^x (or P^x) that governs the blueshift being equal to $1/2$, but we find it to be consistently smaller, and strongly sample dependent. We attribute this to a breakdown of the bimolecular recombination approximation.

II. THEORY

Capacitive charging (CC),^{21–24} BB,^{16–19,25} and state filling^{21,26} are commonly used to explain the blueshift of the emission of type-II QD/QRs with increasing laser power. Band bending at the interface between the QD/QR and surrounding matrix is caused by the electric field from the spatially-separated carrier species. This generates a potential well at the interface, usually assumed to be triangular,²⁷ resulting in a shift of the ground state energy that varies with charge according to²⁸

$$\Delta E_{BB} = \left(\frac{\hbar^2}{2m}\right)^{1/3} \left(\frac{9}{8}\pi\right)^{2/3} \left(\frac{2\pi e^2}{\epsilon_0 \epsilon_r}\right)^{2/3} n_{2D}^{2/3}, \quad (1)$$

where n_{2D} is the carrier density in the proximity of the heterointerface, e is the charge of an electron, $\hbar$ is the reduced Planck constant, m is the electron effective mass, ϵ_0 the permittivity of free space, and ϵ_r the relative permittivity of the semiconductor. This model was originally used to describe blueshifts in type-II quantum wells,^{28,29} but has since been applied to type-II QD systems.^{16–19,25}

However, due to the reduced dimensionality of QD/QRs, capacitive effects must also be considered. The capacitive charging model^{21–24} considers the QD/QR as a nanocapacitor, with a charging energy (δE_{CC}) for each additional charge carrier added after the first

$$\delta E_{CC} = \frac{e^2 d}{2A \epsilon_0 \epsilon_r}, \quad (2)$$

where d is the electron-hole separation and A is the area of the nanostructure. Thus, the total charging energy, ΔE_{CC} , shifts as $\Delta E_{CC} \propto n_h$. In the material system considered here, capacitive charging is the result of hole-hole interactions, so n_h is the number of holes in the QD/QR.

Unfortunately, the carrier density, n_{2D} , and the QD/QR occupancy, n_h , are typically not known, so it is necessary to try to relate them to either the incident laser power or the recombination intensity. The link between carrier density and recombination intensity is made via the bimolecular rate equation,³⁰ which for a bulk semiconductor is

$$\frac{dn_e}{dt} = \frac{dn_h}{dt} = -bn_en_h, \quad (3)$$

where n_e is the electron density, n_h is the hole density, and b is the bimolecular recombination coefficient. From charge neutrality $n_e = n_h$ in a bulk semiconductor, and therefore

$$I = bn^2, \quad (4)$$

where n is the electron or hole density. Hence, since Eq. (4) predicts $I \propto n^2$, the equations for capacitive charging and band bending can now be written in terms of I :

$$\Delta E_{CC} \propto I^{1/2}, \quad (5)$$

and

$$\Delta E_{BB} \propto I^{1/3}. \quad (6)$$

This method of using I to infer n relies on the applicability of Eq. (4) to type-II QD/QRs and is itself derived from Eq. (3) and the charge neutrality condition. The authors are not aware of any studies on its applicability to type-II systems, but theoretical models have indicated that it may not work for type-I QDs.³¹ The 8-band **k.p** calculations presented in Ref. 31 show a reduced optical matrix element for excited states compared with the ground state. Therefore, as the QDs become more charged, the average recombination time increases. Coulomb effects were not taken into account in Ref. 31 as they were predicted to be negligible for the type-I InAs/GaAs QDs investigated in that study. However, this is not the case for the QD/QRs studied here, where strong Coulomb effects dominate the physics, giving rise to the unique properties of type-II systems.^{22,32} The use of Eqs. (5) and (6) to discern the origin of the blueshift in type-II QD/QRs therefore seems questionable. We shall return to this point in Sec. V, but first we briefly describe the samples used in this study, and then go on to present results from a sample in which contributions to the blueshift from capacitive charging and band bending are easily distinguished.

III. EXPERIMENTAL DETAILS

The 11 samples discussed here were grown by molecular beam epitaxy (MBE) on [100] GaAs substrates with different growth conditions. Sample A was grown with a typical method, which produces mainly QRs: A single QR layer was grown by deposition of 2.1 monolayers (MLs) of GaSb at a temperature of 490 °C with a growth rate of 0.3 MLs^{−1} and a V/III ratio of ~ 10 . Next, a 250 nm GaAs cap was grown by first depositing 5 nm of GaAs at 430 °C (cold cap), followed by 245 nm of GaAs at 580 °C. A brief summary of the growth conditions for all samples is presented in Table I. All of the QD/QR samples were formed by the strain-induced Stranski-Krastanov (SK) growth mode, except Sample G, which was grown by migration enhanced epitaxy (MEE). It is known that during growth QDs are initially formed, but after capping a significant number of the GaSb nanostructures are clusters without a well-defined morphology or QRs, with the initial cap temperature and thickness affecting the geometry of the

TABLE I. Growth conditions summary for all samples. For multilayer QD/QRs, the columns to the left of the “# of QR layers” column are the repeated growth steps. Blank cells indicate growth steps which were not carried out for that sample.

Sample	Growth method	GaSb			GaAs cold cap		GaAs spacer		# of QD/QR layers	GaAs cap [final]	
		(ML)	(°C)	V/III ratio for QD/QR	(nm)	(°C)	(nm)	(°C)		(nm)	(°C)
A	SK	2.1	490	10	5	430			×1	245	580
B	SK	2.1	490	10	5	430			×1	250	500
C	SK	2.1	490	10	5	430	30	570	×10	100	570
D	SK	2.1	490	10	5	430	30	500	×10	100	500
E	SK	2.1	490	2	9	430			×1	100	580
F	SK	2.1	490	10	8	450	13	510	×3	300	465
G	MEE	1.5	480	10	10	480	40	580	×10	100	580
H	SK	2.1	490	10	10	490			×1	250	570
I	SK	2.1	490	10	10	490			×1	250	500
J	SK	2.1	490	10	10	490	30	570	×10	100	570
K	SK	2.1	490	10	5	430			×1	250	570

resulting nanostructures.³³ We therefore expect all samples to have a mixture of QDs, QRs, and clusters, with some samples having mostly QDs and some mostly QRs, depending on the growth conditions. However, the distinction between different nanostructure morphologies is not important for our investigation. The models described above and the related discussion below apply equally to QDs and QRs: these two types of nanostructures can be considered as indistinguishable, except that QRs have a reduced volume compared with QDs.

PL measurements of the QD/QRs were carried out at 4.2 K by immersion in liquid helium with a 532 nm continuous-wave laser providing illumination to $\sim 2 \text{ mm}^2$ of the sample via a 200- μm -core optical fibre, allowing the power density to range from $\sim 10^{-2}$ to 10^4 mW/cm^2 . PL emission was collected by a 550- μm -core optical fibre for measurement by a spectrometer and a Peltier-cooled InGaAs array.

IV. DIRECT OBSERVATION OF BLUESHIFTS DUE TO CAPACITIVE CHARGING AND BAND BENDING

The inset of Fig. 2 shows the luminescence from the GaSb/GaAs nanostructures in Sample A, which are known to be mostly QRs.³⁴ The luminescence peak has an intriguing bumpy character and can be fitted with a series of Gaussian sub-peaks of equal width. There are a number of possible explanations for these sub-peaks, but a previous study concluded that each represent ensembles of QRs with specific charge states, i.e., occupancies of between 2 and 8 holes (PL from singly-occupied QRs is of negligible intensity). The ability to observe single-hole charging in ensemble PL in this sample has been attributed to localisation of the electron in the centre of the QRs, which reduces the inhomogeneous broadening. Hints of such substructure have been seen in other QR samples, but it was not possible to clearly resolve the sub-peaks. For the present investigation, this sample represents a remarkable opportunity as it allows us to directly observe the QR occupancy and qualitatively study its variation with laser power. A fully quantitative analysis is not possible because the relationship between occupancy and oscillator strength is not known. Nevertheless, it allows us to unequivocally distinguish the contributions of band bending

and capacitive charging to the blueshift of the centre of mass of the PL. The inset of Fig. 2 shows that the majority of the blueshift is a result of an increase in the intensity of sub-peaks at higher energy (greater occupancy). The energies of the different sub-peaks, each of which represent QRs with a certain hole occupancy, display nearly identical energy shifts with laser power, i.e., sub-peak energy shift is *independent* of occupancy. The inevitable conclusion is that the sub-peak energy shift must be entirely due to a band-bending effect from unconfined charge.³⁴ Most significant is that the laser-power induced blueshift of individual charge-state sub-peaks is, at $\sim 3 \text{ meV}$, an order of magnitude smaller than the shift of the centre of mass of the ensemble peak ($\sim 34 \text{ meV}$). The energy separation of the individual charge-state peaks ($24 \pm 2 \text{ meV}$, see Fig. 2), which is directly attributable to capacitive charging, dominates the blueshift of the ensemble PL.

We now consider the data for this sample in more depth, as it will help to inform our discussion of the other samples

FIG. 2. The minimum emission energy of individual charge-state sub-peaks of Sample A, showing a linear dependence on occupancy, as predicted by capacitive charging. The inset shows the QR PL emission over 5 orders of magnitude of laser power. The numbers indicate the hole occupancy of the charge-state sub-peaks.

in which the charge sub-peaks are not resolved, and of Eqs. (5) and (6). First, we consider capacitive charging. An estimate of the energy shift from capacitive charging is found by substituting values into Eq. (2); we assume QRs with inner and outer radii of 7.5 and 12.5 nm, respectively [estimated from scanning tunnelling microscopy images, such as Fig. 1(b)], $\epsilon_r = 12.9$ and $d = 10$ nm (exciton Bohr radius in GaAs). These values yield a capacitive charging energy of $\delta E_{CC} = 22$ meV per additional hole per QR, which is in good agreement with the experimental value of 24 ± 2 meV. Estimates of $\delta E_{CC} = 13$ meV for larger area (and hence smaller δE_{CC}) GaAsSb/GaAs QDs have been made in the literature.³⁵ To test the $\Delta E_{CC} \propto n_h$ relationship predicted by Eq. (2), the E_0 energy of each charge-state sub-peak, i.e., the inferred peak energy at zero laser power, where there is no contribution from band bending, is plotted against hole occupancy in Fig. 2. By analysing the data in this way, all contributions from band bending are removed, and only capacitive charging contributes to the differences in energy between the data points. Fig. 2 shows that the capacitive charging model, $\Delta E_{CC} \propto n_h$, works very well. Next, to see if the magnitude of the energy shift of the sub-peaks matches that predicted by the band bending model, values for GaAs were substituted into Eq. (1). With an electron effective mass of $0.067m_0$ and relative permittivity of 12.9, a change in n_{2D} of $1 \times 10^9 \text{ cm}^{-2}$ is required to replicate the band-bending energy shift seen in our data, which is very reasonable for the applied laser-power range. This provides further evidence that the contribution of band bending is small and that capacitive charging dominates the blueshift in type-II QD/QRs.

State filling is another possible source of energy shift for emitted photons, i.e., recombination from higher-energy quantised holes levels. However, this was already excluded as a possible origin of the sub-peaks in Sample A.³⁴ Rather, we believe that the PL is strongly dominated by recombination from the hole ground-state in the QR. As a result, the observed energy separation of sub-peaks is due to the energy shift of the ground state by capacitive charging. This results in the astonishingly equally-spaced PL sub-peaks that are shown in Fig. 2.

V. DEPENDENCE OF THE BLUESHIFT ON EMISSION INTENSITY

Hole occupancy of QD/QR ensembles is usually not accessible from PL measurements, so another PL parameter is necessary to infer the carrier density or QD/QR occupancy, and the incident laser power, P , is frequently used as a convenient choice. To arrive at $P \propto n_h^2$, two assumptions must be made: Firstly that $P \propto I$, and also that $I \propto n_h^2$. The second of these assumptions is the main focus of the remainder of this paper and is discussed in more detail later in this section, but we first turn our attention to the validity of $P \propto I$.

Since we are considering a type-II QD/QR system, there will be increasing Coulomb repulsion of holes from the nanostructures as they become charged. Holes may also occupy other regions of the sample (e.g., WL, bulk semiconductor, impurities or defect states) at higher (or lower) laser powers. Thus, a non-linear transfer rate of holes to the

QD/QRs with increasing excitation is likely. Fig. 3 shows a log-log plot of I vs P for Sample I. A linear relationship with a gradient of 1 that is typical of excitonic recombination is observed at low laser powers, but at higher laser powers, the data become increasingly sub-linear, consistent with reduced carrier transfer into the QD/QRs. This sub-linear region constitutes a significant portion of the laser power range investigated. Similar behaviour was seen for all samples investigated. Furthermore, our set-up uses optical fibres: The size of the laser spot on the sample is $\sim 1\text{--}2$ mm in diameter, meaning that laser power densities in our experiments are on the lower side of those typically used. For these reasons, it is clear that the assumption that $P \propto I$ can fail and the use of QD/QR PL emission intensity, I , as a measure of n_h in all experiments looks preferable, although bimolecular recombination is still implicitly assumed.

A second issue is that it may be difficult to distinguish between an exponent of $x = 1/3$ (band bending) and $x = 1/2$ (charging), if data are explicitly plotted as ΔE versus $P^{1/3}$ or $I^{1/3}$, especially if the range of laser power is not very large. In this investigation, we varied the laser power over 5–6 orders of magnitude for many samples. We suggest that a log-log analysis, using emission intensity rather than excitation power, is the best method to ascertain the exponent, x , without the need for prior assumptions of its value.

To do this, the minimum transition energy (E_0) must first be found and subtracted from the raw QD/QR emission energy data. E_0 is the energy between the QD/QR ground-state and the GaAs conduction band edge, under zero excitation power, including any additional charging energy due to the presence of holes from (unintentional) doping.^{24,34} The QD/QR peak emission energy is taken from the PL spectra [Fig. 4(a)] and plotted against the integrated peak intensity. E_0 is then found by extrapolating a linear fit to the lowest intensity data points (Fig. 4(b) inset), and subsequently subtracted from the absolute QD/QR peak energy values to yield the energy shift, ΔE . Finally, a linear fit is used on the resulting log-log graph [see Fig. 4(b)] to extract the exponent, x .

We start with Sample A, applying this analysis to each of the sub-peaks and also the centre of mass of the PL. The

FIG. 3. Log-log plot of sample emission intensity versus incident laser power for Sample I. The data show good agreement with the linear fitting at low laser power, but become sub-linear at high power.

FIG. 4. (a) A selection of PL spectra from Sample B at different excitation laser powers. Numbers to the left of spectra indicate the PL intensity before normalisation. The dashed line is a guide to the eye which shows the peak positions. (b) QR peak energy shift, ΔE , plotted against peak intensity for the same sample. A line is fitted to the linear region to extract the exponent. The inset shows the low-intensity-data-point fitting used to find E_0 , allowing ΔE to be plotted in the main figure.

results for the ~ 3 meV blueshift of the sub-peaks, which we have shown is due to band bending, are shown in the inset of Fig. 5. It can be seen that, within uncertainty, an exponent of $1/3$ is found for all sub-peaks, exactly as expected. The results for the much larger blueshift of the centre of mass of the PL for all samples are shown in the main part of Fig. 5. There is considerable variation, but we can make the following observations. (1) Given the order of magnitude difference in the size of the band bending and charging blueshifts in Sample A, we can make the reasonable assumption that charging is the dominant cause of the blueshift in all samples, i.e., we expect to see $x = 1/2$. Yet in every single case it is lower. (2) More specifically, we know that for Sample A the blueshift of the ensemble PL peak is due to capacitive charging, but we see a lower exponent that is, coincidentally, $1/3$. (3) In the case of Sample J, the exponent lies somewhere between $1/3$ and $1/2$, so band-bending is excluded as the dominant mechanism, but the exponent falls short of what we expect for charging. (4) For all the other samples, the exponent is even lower, $< 50\%$ of what we would expect. (5) Even if we are sceptical about charging dominating the blueshift in all samples, the exponents for these samples are systematically low. Thus, given that we have studied a large number of samples,

FIG. 5. Exponents for Samples A-K. Dashed lines show the expected exponents for CC and BB. Uncertainties are estimated from fitting straight lines in plots equivalent to Fig. 2. The inset shows the exponents for the sub-peaks of Sample A.

grown in a variety of conditions, and applied a very careful and rigorous analysis of the data, the inescapable conclusion is that the exponent, x , in $\Delta E \propto I^x$ cannot be used to distinguish between band bending and capacitive charging. This strongly implies that there is a flaw in the derivation of Eqs. (5) and (6). We suggest that this is the breakdown of the bimolecular recombination approximation, i.e., I is not proportional to n_h^2 for type-II QD/QRs.

VI. DISCUSSION

We have shown that the exponent, x , in the power law governing the blueshifts of the centre of mass of the PL in type-II QD/QRs is systematically lower than expected. It is likely that a new form of the bimolecular recombination equation [Eq. (3)] is required when describing type-II QD/QRs and that the charge neutrality condition, $n_e = n_h$, does not hold for such systems. Both of these would modify the n dependence of Eq. (4).

It has previously been proposed that the bimolecular recombination coefficient, b , for QDs should be modified to include an n dependence.³¹ In contrast to the type-I QDs of Ref. 31 where an *increased* carrier lifetime for increased occupancy was discussed, but where Coulomb effects were expected to be negligible, we expect a *decreased* average carrier lifetime with increased occupancy in type-II QD/QRs. Physically, this could be caused by tighter electron binding and an increased recombination rate at higher excitation powers. Indeed, previous work has shown that charged type-II QDs can exhibit tighter electron binding in magneto-PL experiments,^{22,36} and reduced carrier lifetime in time-resolved PL.²⁶ Such effects would increase the emission intensity of highly-charged QD/QRs, leading to the reduced exponents observed. However, this explanation does not clarify why the correct exponent was found for band bending in Sample A. Unlike capacitive charging, it is not possible to confirm the n_{2D} dependence of band bending [Eq. (1)] without the use of the bimolecular rate equation. Therefore, the current forms of both the band bending and the bimolecular rate equations may not be applicable to this system, and

possibly only coincidentally give the expected $1/3$ exponent dependence (inset to Fig. 5).

The notion that QD/QR hole occupancy plays an important role in the exponent may explain the striking deviation of Sample J from the $x < 1/3$ trend of the data in Fig. 5. By briefly returning to Sample A, a possible explanation is postulated as follows: The very low power PL spectra of Sample A (inset to Fig. 2) have a maximum in intensity at a QD/QR occupancy of 4 holes. These holes are believed to originate from unintentional background doping and act to increase the ground-state transition energy compared with an uncharged dot. Sample J has the lowest E_0 value reported for any GaSb/GaAs QD/QR sample³⁷ and, during growth, this sample was exposed to high temperatures for the longest time, due to the hot GaAs cap temperature and 10 layers of QR growth. It has been shown that higher temperature MBE growth of GaAs decreases the incorporation of unintentional p-dopants.³⁸ Therefore the lower E_0 value for Sample J may indicate less background doping, with fewer holes in the QRs, a reduced recombination rate, and thus a higher exponent than any of the other samples.

Further analysis was carried out in an attempt to find any correlations between x and any other properties of the samples. However no clear relationships between x and QR intensity, growth conditions or sample structure were found. It is possible that subtle variations in growth conditions, leading to differences in nanostructure types/geometries,^{33,39} as well as different defect/impurity densities between samples, account for the range of exponents observed.

Before concluding, we would like to briefly comment on some wider implications of our results. The first is that the inability to apply the bimolecular rate equation [Eq. (3)], and subsequently Eq. (4), to type-II QD/QR systems could have far-reaching consequences for optical analysis of device performance. For example, an exponent analysis of electroluminescence (EL) measurements is commonly used when characterising a light emitting diode or laser device to determine the dominant recombination mechanism at different temperatures.^{40,41} We expect that the failure of Eq. (4) will need to be considered when using such an approach. The second is that different values of x can have consequences for device performance. In a type-II solar cell, for example, it would be desirable to have a larger x value (e.g., Sample J), such that radiative recombination is suppressed. However in a type-II laser device, where strong emission and good wavelength stability are preferred, a lower x value is required. This would increase the radiative recombination rate, simultaneously increasing the emission intensity and slowing the shift of the emission energy with increasing carrier generation rate.

VII. CONCLUSIONS

We have studied the laser-excitation-power-induced blueshifts of type-II QD/QRs. The ability to distinguish between band bending and capacitive charging as mechanisms behind the blueshift in Sample A leads to the conclusion that in type-II QD/QR samples capacitive charging dominates. Analysis of the energy separation and laser-

power-induced energy shifts of charge state sub-peaks shows that the simple capacitive charging model accurately describes our data. However when the more generalizable $\log(\text{intensity})$ vs $\log(\text{energy})$ analysis was applied, discrepancies were found. We conclude that the bimolecular recombination approximation, which has widespread use in optical properties of semiconductors, is not applicable to type-II QD/QRs. Further modification of the QR radiative term is required, such that the QRs become more efficient radiative centres as they become more highly charged. This may have benefits for the wavelength stability and emission intensity of lasers made from GaSb/GaAs QRs, but may also point to reduced efficiency in type-II solar cells, unless careful consideration is given to radiative recombination rates.

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- ¹D. Bimberg, N. Kirstaedter, N. N. Ledentsov, Z. I. Alferov, P. S. Kopev, and V. M. Ustinov, *IEEE J. Sel. Top. Quantum Electron.* **3**, 196 (1997).
- ²A. J. Nozik, *Physica E* **14**, 115 (2002).
- ³A. J. Shields, *Nat. Photonics* **1**, 215 (2007).
- ⁴D. Bimberg, M. Grundmann, and N. Ledentsov, *Quantum Dot Heterostructures* (Wiley, New York, 1999).
- ⁵T. Y. Gu, M. A. El-Emawy, K. Yang, A. Stintz, and L. F. Lester, *Appl. Phys. Lett.* **95**, 261106 (2009).
- ⁶A. Marent, T. Nowozin, M. Geller, and D. Bimberg, *Semicond. Sci. Technol.* **26**, 014026 (2011).
- ⁷M. Hayne, R. J. Young, E. P. Smakman, T. Nowozin, P. Hodgson, J. K. Garleff, P. Rambabu, P. M. Koenraad, A. Marent, L. Bonato, A. Schliwa, and D. Bimberg, *J. Phys. D: Appl. Phys.* **46**, 264001 (2013).
- ⁸M. Geller, A. Marent, T. Nowozin, D. Bimberg, N. Akcay, and N. Oncan, *Appl. Phys. Lett.* **92**, 092108 (2008).
- ⁹T. Nowozin, A. Marent, L. Bonato, A. Schliwa, D. Bimberg, E. P. Smakman, J. K. Garleff, P. M. Koenraad, R. J. Young, and M. Hayne, *Phys. Rev. B* **86**, 035305 (2012).
- ¹⁰T. Nowozin, L. Bonato, A. Hogner, A. Wiengarten, D. Bimberg, W.-H. Lin, S.-Y. Lin, C. J. Reyner, B. L. Liang, and D. L. Huffaker, *Appl. Phys. Lett.* **102**, 052115 (2013).
- ¹¹R. B. Laghumavarapu, A. Moscho, A. Khoshakhlagh, M. El-Emawy, L. F. Lester, and D. L. Huffaker, *Appl. Phys. Lett.* **90**, 173125 (2007).
- ¹²P. J. Carrington, M. C. Wagener, J. R. Botha, A. M. Sanchez, and A. Krier, *Appl. Phys. Lett.* **101**, 231101 (2012).
- ¹³C. F. Klingshirn, *Semiconductor Optics* (Springer, Berlin, 1997).
- ¹⁴T. Nuytten, M. Hayne, B. Bansal, H. Y. Liu, M. Hopkinson, and V. V. Moshchalkov, *Phys. Rev. B* **84**, 045302 (2011).
- ¹⁵S. Fafard, Z. R. Wasilewski, C. N. Allen, D. Picard, M. Spanner, J. P. McCaffrey, and P. G. Piva, *Phys. Rev. B* **59**, 15368 (1999).
- ¹⁶J. Tatebayashi, A. Khoshakhlagh, S. H. Huang, G. Balakrishnan, L. R. Dawson, and D. L. Huffaker, *Appl. Phys. Lett.* **90**, 261115 (2007).
- ¹⁷D. Alonso-Alvarez, B. Alen, J. M. Garcia, and J. M. Ripalda, *Appl. Phys. Lett.* **91**, 263103 (2007).
- ¹⁸P. J. Simmonds, R. B. Laghumavarapu, M. Sun, A. D. Lin, C. J. Reyner, B. L. Liang, and D. L. Huffaker, *Appl. Phys. Lett.* **100**, 243108 (2012).
- ¹⁹Y. I. Mazur, V. G. Dorogan, G. J. Salamo, G. G. Tarasov, B. L. Liang, C. J. Reyner, K. Nunna, and D. L. Huffaker, *Appl. Phys. Lett.* **100**, 033102 (2012).
- ²⁰W. H. Lin, K. W. Wang, S. W. Chang, M. H. Shih, and S. Y. Lin, *Appl. Phys. Lett.* **101**, 031906 (2012).
- ²¹L. Muller-Kirsch, R. Heitz, A. Schliwa, O. Stier, D. Bimberg, H. Kirmes, and W. Neumann, *Appl. Phys. Lett.* **78**, 3908 (2001).
- ²²B. Bansal, S. Godefroy, M. Hayne, G. Medeiros-Ribeiro, and V. V. Moshchalkov, *Phys. Rev. B* **80**, 205317 (2009).

- ²³K. Gradkowski, T. J. Ochalski, D. P. Williams, S. B. Healy, J. Tatebayashi, G. Balakrishnan, E. P. O'Reilly, G. Huyet, and D. L. Huffaker, *Phys. Status Solidi B* **246**, 752 (2009).
- ²⁴M. Hayne, O. Razinkova, S. Bersier, R. Heitz, L. Muller-Kirsch, M. Geller, D. Bimberg, and V. V. Moshchalkov, *Phys. Rev. B* **70**, 081302 (2004).
- ²⁵F. Hatami, M. Grundmann, N. N. Ledentsov, F. Heinrichsdorff, R. Heitz, J. Bohrer, D. Bimberg, S. S. Ruvimov, P. Werner, V. M. Ustinov, P. S. Kop'ev, and Z. I. Alferov, *Phys. Rev. B* **57**, 4635 (1998).
- ²⁶K. Gradkowski, T. J. Ochalski, N. Pavarelli, H. Y. Liu, J. Tatebayashi, D. P. Williams, D. J. Mowbray, G. Huyet, and D. L. Huffaker, *Phys. Rev. B* **85**, 035432 (2012).
- ²⁷J. H. Davies, *The Physics of Low-Dimensional Semiconductors* (Cambridge University Press, 2006).
- ²⁸N. N. Ledentsov, J. Bohrer, M. Beer, F. Heinrichsdorff, M. Grundmann, and D. Bimberg, *Phys. Rev. B* **52**, 14058 (1995).
- ²⁹Y. S. Chiu, M. H. Ya, W. S. Su, and Y. F. Chen, *J. Appl. Phys.* **92**, 5810 (2002).
- ³⁰E. F. Schubert, *Light-Emitting Diodes* (Cambridge University Press, 2003).
- ³¹A. D. Andreev and E. P. O'Reilly, in *Physica Status Solidi C—Conferences and Critical Reviews*, edited by M. Stutzmann (Wiley-VCH Verlag GmbH, Weinheim, 2005), Vol. 2, No. 4, p. 1374.
- ³²B. Bansal, M. Hayne, M. Geller, D. Bimberg, and V. V. Moshchalkov, *Phys. Rev. B* **77**, 241304 (2008).
- ³³E. P. Smakman, J. K. Garleff, R. J. Young, M. Hayne, P. Rambabu, and P. M. Koenraad, *Appl. Phys. Lett.* **100**, 142116 (2012).
- ³⁴R. J. Young, E. P. Smakman, A. M. Sanchez, P. Hodgson, P. M. Koenraad, and M. Hayne, *Appl. Phys. Lett.* **100**, 082104 (2012).
- ³⁵M. Geller, C. Kapteyn, L. Muller-Kirsch, R. Heitz, and D. Bimberg, *Appl. Phys. Lett.* **82**, 2706 (2003).
- ³⁶M. Hayne, J. Maes, S. Bersier, V. V. Moshchalkov, A. Schliwa, L. Muller-Kirsch, C. Kapteyn, R. Heitz, and D. Bimberg, *Appl. Phys. Lett.* **82**, 4355 (2003).
- ³⁷P. J. Carrington, R. J. Young, P. D. Hodgson, A. M. Sanchez, M. Hayne, and A. Krier, *Cryst. Growth Des.* **13**, 1226 (2013).
- ³⁸C. H. Goo, W. S. Lau, T. C. Chong, L. S. Tan, and P. K. Chu, *Appl. Phys. Lett.* **68**, 841 (1996).
- ³⁹M. A. Kamarudin, M. Hayne, R. J. Young, Q. D. Zhuang, T. Ben, and S. I. Molina, *Phys. Rev. B* **83**, 115311 (2011).
- ⁴⁰A. Krier and V. V. Sherstnev, *J. Phys. D: Appl. Phys.* **36**, 1484 (2003).
- ⁴¹T. Higashi, S. J. Sweeney, A. F. Phillips, A. R. Adams, E. P. O'Reilly, T. Uchida, and T. Fujii, *IEEE J. Sel. Top. Quantum Electron.* **5**, 413 (1999).