Fast relaxation of hot carriers by impact ionization in semiconductor nanocrystals: Role of defects

Guy Allan and Christophe Delerue
Département ISEN, Institut d'Electronique de Microélectronique et de Nanotechnologie, UMR CNRS 8520, 41 Boulevard Vauban, F-59046 Lille Cedex, France
(Received 25 March 2009; published 26 May 2009)

We present calculations predicting that defects at the surface of semiconductor nanocrystals have a strong influence on the dynamics of hot carriers after photoexcitation. The relaxation of excited carriers by impact ionization of carriers trapped on deep levels is efficient, in particular in the presence of a band of defect states in the gap. Impact ionization of defects can also induce single-carrier multiplication but carriers generated in this way have a 1–100 ps lifetime due to multiphonon capture by the defects. These results are used to discuss recent experimental studies on carrier relaxation and multiplication in nanocrystals.

DOI: 10.1103/PhysRevB.79.195324 PACS number(s): 78.67.Bf, 73.22.−f, 78.40.Fy, 78.47.−p

I. INTRODUCTION

Semiconductor nanocrystals receive a great deal of attention due to their properties, which can be tuned via their shape and their size, which make them attractive for various applications, including optoelectronic devices,[1] solar cells,[2] or biological detection.[3] Recently, intense research has focused on the dynamics of electrons and holes after optical excitation at energies well above the nanocrystal band gap. In that case, interesting phenomena are expected due to significant enhancement in carrier-carrier Coulomb interactions induced by the strong confinement.[4] In particular, many experiments reveal that excited carriers quickly relax to lower-energy states in spite of a discrete energy spectrum.[5–9] Efficient relaxation of hot carriers in nanocrystals is often explained by the electron-hole scattering mechanism in which the electron transfers its excess energy to the hole and the hole can relax via phonon emission due to the high density of hole states.[7,10–12] But this interpretation is largely debated,[8,9,13] in particular because fast relaxation of the electron is observed in the absence of hole.[6,7,13] In addition, several works have revealed that the relaxation rate of excited carriers strongly depends on the passivation and on the capping of the nanocrystals.[13,14]

Another dynamical effect that presently receives considerable attention is carrier multiplication (CM) and consequently multiexciton generation which consists in the generation of multiple electron-hole pairs by a single photon. Since the first report on efficient CM in nanocrystals by Schaller *et al.*,[15] a number of experimental studies confirmed the occurrence of CM in PbSe,[15–19] PbS,[16] CdSe,[19,20] InAs,[21,22] and Si (Ref. 23) nanocrystals. CM is usually monitored in pump-probe experiments by its effect on transient absorption,[15,16] luminescence,[20,24] and terahertz conductivity.[21] It is also revealed in photoconductivity.[18] But the existence of efficient CM in nanocrystals remains largely discussed.[21,24–29] Recent works on PbSe,[26,27] CdSe, CdTe,[24] and InAs (Refs. 21 and 25) nanocrystals concluded that the CM efficiency is either negligible or much smaller than in early reports. In addition, recent theoretical works have shown that relaxation of excited carriers by impact ionization may be at the origin of some CM in nanocrystals at high photon energy[28–31] but cannot explain the highest yields reported experimentally.[28,29]

From these results, it is clear that the current knowledge of the dynamics of hot carriers in nanocrystals is far from being complete and that it is important to identify all the mechanisms at the origin of fast relaxation and CM in nanocrystals. In this paper, we show that surface defects can have an important effect on these processes due to the strong electron-electron interactions. Surface states are expected in nanocrystals due to high surface-to-volume ratio; they are studied in a large number of works[32–37] and are invoked to explain nanocrystal blinking.[38] It is well known that defects can capture carriers from the bands but their effect on the carrier relaxation has not been evaluated so far. Therefore we present calculations of the impact ionization rates in the presence of deep defect levels.

II. METHODOLOGY

We consider an electron or a hole excited in a nanocrystal and its relaxation by impact ionization: the excited carrier decays to a lower-energy state and excites an electron from an occupied state to an unoccupied one (Fig. 1). In the usual impact ionization mechanism [Fig. 1(a)], the electron is ex-

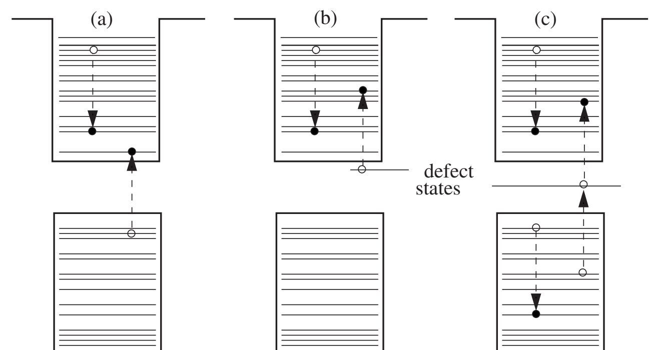

FIG. 1. (a) Schematics of the impact ionization process for the relaxation of a hot electron and the subsequent excitation of an electron from the valence band to the conduction band. The process for the relaxation of an excited hole is symmetric. (b) Same process but involving an electron on a deep level instead of a valence-band electron. (c) Generation of an exciton via a deep level following the relaxation of an electron and a hole in cascade.

 ©2009 The American Physical Society

cited from a valence state to a conduction one; the relaxation generates an electron-hole pair.[15,16] The main objective of our work is to consider, in addition to this process, other mechanisms in which, for example, the relaxation of the carrier excites an electron from a deep level to the conduction band [Fig. 1(b)] or, symmetrically, excites a valence electron to an empty deep level. For all these processes corresponding to transitions between initial states $|i\rangle$ and final states $|f\rangle$ of the electronic system, we calculate the relaxation lifetime τ using the Fermi golden rule,

$$1/\tau = 2\pi |V_{if}|^2 \rho_f(E)/\hbar, \tag{1}$$

where $\rho_f(E)$ is the density of final states at the energy E and V_{if} is the transition matrix element of the screened Coulomb interaction. This procedure is justified in Refs. 28 and 29.

We consider the case of Si nanocrystals because their surface can be passivated by hydrogen atoms and, consequently, surface dangling bond defects are created in a well-controlled manner just by removing some of these hydrogen atoms. We calculate the electronic structure of the nanocrystals in tight binding as described in Ref. 39. This method is very efficient to simulate the electronic structure of semiconductor nanocrystals[40] and gives the possibility to apply an intra-atomic potential U on each surface atom with a dangling bond to adjust the deep level position in the gap.

Details on the calculation method are given in Refs. 28 and 29. For each initial state $|i\rangle$ corresponding to an excited carrier, either a hole in the valence band (with negative energy E and with the zero energy corresponding to the top of the bulk valence band) or an electron in the conduction band ($E>0$), we compute the relaxation lifetime from Eq. (1). In principle, $\rho_f(E)$ is a sum of Dirac functions but we have broadened each peak by a Gaussian with a width of 5 meV to simulate the coupling of the electronic states to their environment. This broadening can be easily justified by the electron vibration coupling which is enhanced in nanocrystals and which is even stronger on defects.[40] Therefore the value of 5 meV can be safely considered as a lower bound for the broadening.[40,41]

III. RESULTS

The lifetimes calculated with $U=-0.8$ eV are presented for two nanocrystal sizes in Fig. 2 as a function of the energy E of the excited carrier. In each case, we compare two situations corresponding to the perfectly passivated nanocrystal and to the nanocrystal with two dangling bonds, respectively. Due to the proximity of the two dangling bonds in a nanocrystal, there is always a small coupling between the two surface states leading to two deep levels in the gap (at 0.64 and 1.08 eV for a diameter of 2.2 nm and at 0.66 and 0.94 eV for a diameter of 2.7 nm). The lowest state is fully occupied; the highest one is unoccupied.

Figure 2 shows that there is an energy region (around $E \approx 0$) where the impact ionization is energetically impossible, i.e., when the carrier excess energy is too small to induce an electronic transition. At high excess energy ($E \gtrsim 6$ eV or $E \lesssim -4$ eV), the results obtained with and without surface states cannot be distinguished, meaning that the relaxation occurs by usual impact ionization leading to the generation of an electron-hole pair. But, at lower excess energy, the lifetime is much shorter in the presence of dangling bonds because the main relaxation mechanism is the impact ionization via the deep levels.

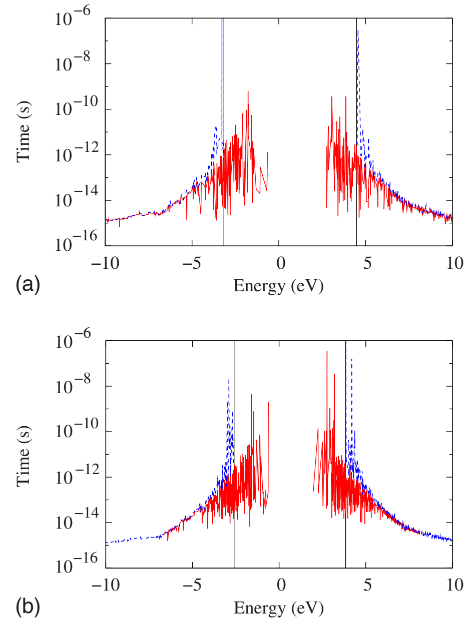

FIG. 2. (Color online) Relaxation lifetime (τ) versus the energy of the excited carrier in (a) 2.2 and (b) 2.7 nm Si nanocrystals, in the presence (solid red line) or in the absence (dashed blue line) of two dangling bond states. The zero of energy corresponds to the top of the bulk valence band: positive (negative) energies correspond to excited electron (hole) states. The vertical bars indicate the thresholds for impact ionization in the absence of surface states.

There is also a range of energy (between the two vertical bars in Fig. 2) where impact ionization is allowed in the presence of defects whereas it is forbidden in their absence. The reason is that less energy is required to excite a carrier from/to a deep state than through the gap, and therefore the density of final states presents thresholds at lower excess energy as shown in Fig. 3. Obviously, these thresholds for impact ionization via surface defects depend on the position

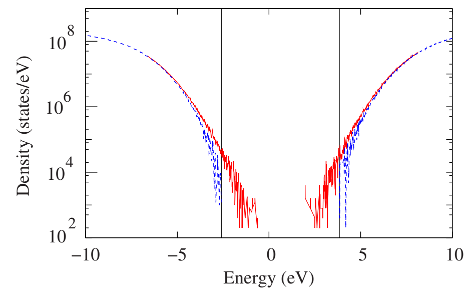

FIG. 3. (Color online) Density of final states $\rho_f(E)$ as a function of the energy E of the excited carrier in a 2.7 nm Si nanocrystal, in the presence (solid red line) or in the absence (dashed blue line) of two dangling bond states. The zero of energy corresponds to the top of the bulk valence band: positive (negative) energies correspond to excited electron (hole) states. The vertical bars indicate the thresholds for impact ionization in the absence of surface states.

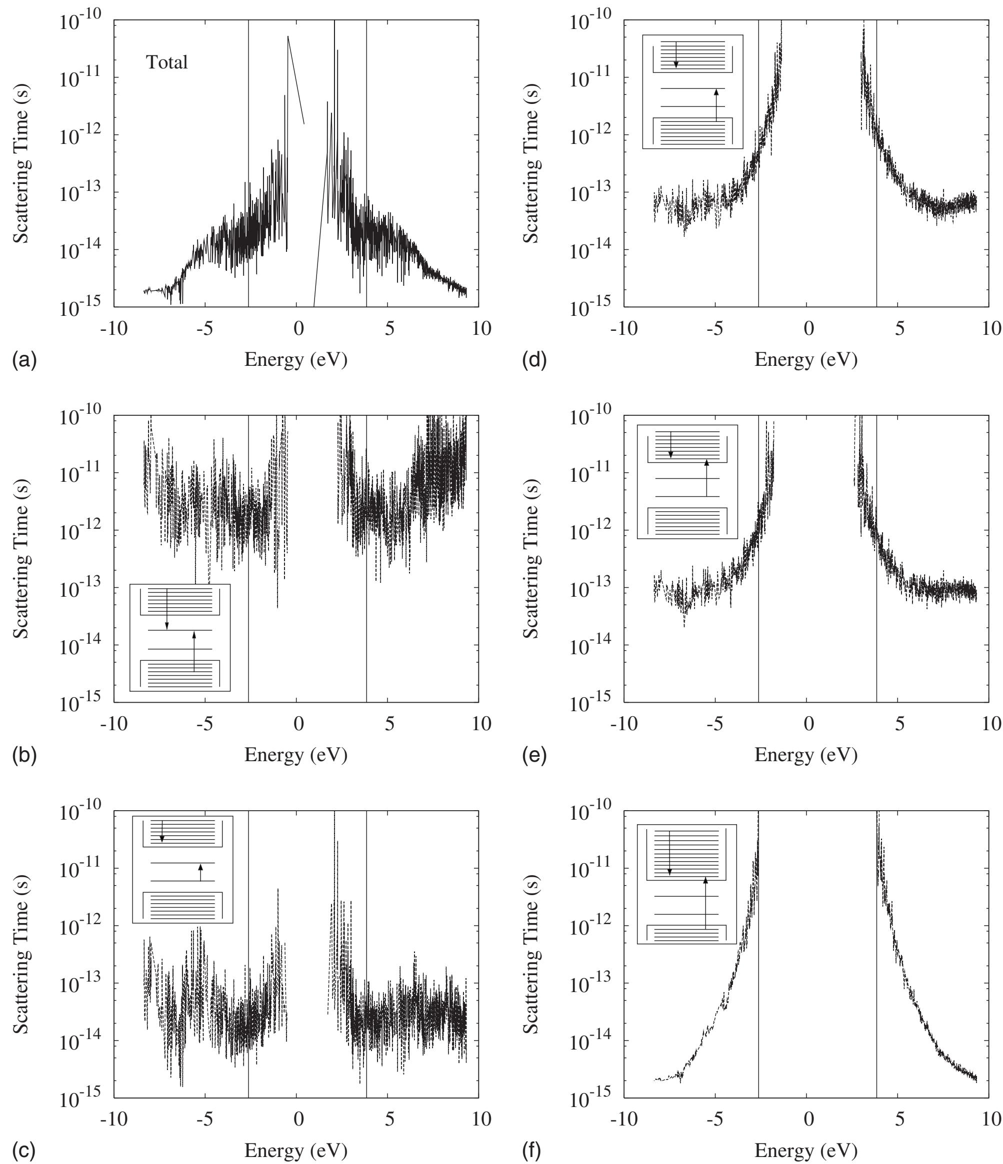

FIG. 4. Relaxation lifetime (τ) versus the energy of the excited carrier in a 2.7 nm Si nanocrystal with ten dangling bond states at the surface. The zero of energy corresponds to the top of the bulk valence band: positive (negative) energies correspond to excited electron (hole) states. The lifetimes corresponding to different channels for the relaxation are shown in (b)–(f), while the total lifetime is presented in (a).

of the deep levels in the gap but we have checked that the curves remain quite similar when we vary the value of U. For example, a variation of 1 eV of U leads to a $\sim$0.5 eV shift of the deep level, the thresholds are shifted accordingly, but the lifetime versus energy remains almost unchanged in average.

The impact ionization of the electrons on the deep levels is a very efficient process as shown by comparing $\tau(E)$ (Fig. 2) and the density of final states $\rho_f(E)$ (Fig. 3). At high excess energy, when the usual impact ionization process is the most efficient, the relaxation rate $(1/\tau)$ is basically proportional to ρ_f because the matrix element $|V_{if}|^2$ is in average approximately constant (see discussions in Refs. 28 and 29 and Fig. 2 of Ref. 29). But this is not the case at low excess energy where τ varies much less than ρ_f. We interpret this result by the strong localization of the surface states which influences the matrix elements of the electron-electron Coulomb interaction.

The relaxation lifetime in the presence of two dangling bonds (Fig. 2) is found—in average—between 10 fs and 10 ps. The lifetime at low excess energy tends to become smaller when the number of surface defects increases. To illustrate this behavior, we consider in the following a nanocrystal with ten dangling bonds at the surface. In that case, there is a strong coupling between the dangling bonds leading to the formation of ten deep levels scattered in the gap (only five are occupied by electrons). This situation could be considered as extreme but the formation of surface state bands was considered in previous works,[37] in particular to explain quantum dot blinking.[38] Much shorter lifetime (i.e., largely subpicosecond) is obtained with ten defects [Fig. 4(a)]. In order to analyze this situation in depth, we present

in Figs. 4(b)–4(f) the calculated lifetimes for different relaxation channels that contribute to the overall lifetime of Fig. 4(a). The usual impact ionization process [Fig. 4(f)] leading to the generation of an exciton remains the most efficient one at high carrier excess energy ($E<5$ eV or $E>6$ eV). At lower excess energy, other processes involving deep states become more efficient. The most efficient one corresponds to the relaxation of the electron in the conduction band (or symmetrically the hole in the valence band) and the subsequent excitation of an electron within surface states [Fig. 4(c)]. The processes shown in Figs. 4(d) and 4(e) leading to the excitation of an electron between a deep state and a band are also quite efficient.

IV. DEFECTS AND FAST RELAXATION OF EXCITED CARRIERS

The main result of our calculations is that fast relaxation by impact ionization is predicted in a wide range of energy in the presence of surface defects, in particular when surface states tend to form a band in the gap, a situation which was considered in a model explaining the quantum dot blinking.[38] Subpicosecond lifetimes agree well with the reported values for the relaxation of hot carriers in nanocrystals.[8,9,19,42] They arise from the combination of two effects: (1) the opening of new channels for the relaxation and (2) the strong electron-electron interactions in nanocrystals. The influence of defects can be reduced by a better passivation, for example, by the growth of shell made of a wide-gap semiconductor. Recent works have shown that the photoluminescence does not blink in nanocrystals with a very thick shell.[43,44] In addition, the relaxation lifetime can be considerably increased in the presence of a shell, at the condition that the hole is removed to avoid fast relaxation by electron-hole scattering.[14]

V. DEFECTS AND CARRIER MULTIPLICATION

Let us discuss the possible role of surface defects on recent experiments showing CM.[15–26] All these experiments indirectly probe the population of carriers at the band edges. They indicate a rapid increase in this population after a pump pulse but hardly distinguish between carriers obtained by the generation of excitons and those obtained by transitions from surface defects [Figs. 4(d) and 4(e)]. In transient absorption experiments,[4] pump-pulse-induced absorption changes are probed with a second time-delayed pulse that is tuned to the lowest-energy exciton transition. The resonant absorption signal is not a direct measure of the electron-hole population since it relates to single-particle state filling (in contrast to transient photoluminescence experiments[24]). For example, a complete filling of either electron or hole band-edge states is sufficient to quench the resonant absorption.

If the impact ionization can induce single-carrier CM, it cannot directly generates excitons [Fig. 1(b)]. However, two impact ionization processes in cascade in which a deep level acts as an intermediate state generate an exciton [Fig. 1(c)]. Impact ionization of deep defects could be also effective in photoconductivity experiments on assemblies of nanocrystals.[18] Carriers trapped at surface defects do not contribute to the current but the photocurrent could be induced by the emission of these carriers to the more delocalized band-edge states of the nanocrystals.

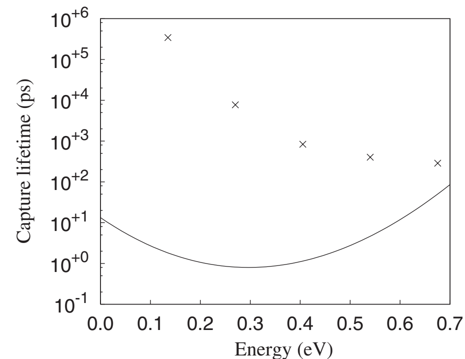

FIG. 5. Lifetime for the relaxation of an electron from the lowest conduction state to a deep defect level as a function of its ionization energy E_i. Two processes are compared: multiphonon capture (solid line) or Auger relaxation (crosses).

VI. CAPTURE OF IONIZED CARRIERS BY SURFACE DEFECTS

Another signature of CM is the fast component (10–100 ps) of the transient absorption signal.[15–26] It is usually interpreted—with convincing arguments—by the fast decay of multiexciton population due to Auger effect.[4] We show in the following that, after emission of carriers from deep levels by impact ionization, the multiphonon capture of the carriers by the surface defects could also contribute to the fast component. We calculate the lifetime as detailed in our previous works.[40,45] We consider a nanocrystal diameter of 2.7 nm and a single defect characterized by an ionization energy E_i, a capture cross section of 10^{-15} cm^2 for $E_i=0.3$ eV, and a relaxation energy (Franck-Condon shift) of 0.3 eV. These data for the electron-vibration coupling are those known for the Pb defect at Si-SiO_2 interface, thus representing typical values for surface defects.[40,45] Figure 5 shows that the capture lifetime is between 1 and 100 ps in a wide range of energy E_i, which is close to the measured lifetimes for the fast component. We have also considered an Auger-type process when there are two electrons on the lowest conduction state: one electron decays to the defect state and the second one is excited to higher energy. We calculate the lifetime as function of E_i using the same method as for the impact ionization except that, for the sake of comparison, we consider for the broadening the same electron-phonon coupling as for the multiphonon capture. We obtain that this Auger-type process is less efficient than the multiphonon capture in this situation (Fig. 5).

VII. CONCLUSION

In conclusion, our work suggests that surface defects in nanocrystals play an important role in the dynamics of excited carriers because they open new efficient channels for the relaxation by impact ionization. The thresholds for impact ionization are shifted to lower excess energy above

which the relaxation rate is strongly enhanced. When there is a defect band in the gap of the nanocrystals,[38] the relaxation by impact ionization can be associated with the excitation of an electron between defect levels. Another efficient channel leads to single-carrier multiplication through the emission of a carrier from a deep level to a band state. Multiexciton generation is also possible if defect states act as intermediate levels [Fig. 1(b)]. Multiexciton generation efficiency could be also improved by surface defects if we imagine, as in the case of oxidized porous silicon,[46] occupied and unoccupied electron levels induced by defects showing a gap sufficiently large to be useful in photovoltaic applications.

Another result of our work is that the 1–100 ps lifetime of generated carriers could be also ascribed to the multiphonon capture by defects which were ionized by impact ionization. A more general conclusion of our study is that the dynamics of excited carriers becomes very complex in the presence of defects. Due to strong electron-electron interactions, which are already at the origin of Auger[4] and electron-hole scattering[7,10–12] effects, many processes involving surface defects become efficient. All these effects can be reduced by the growth of a large shell in core-shell nanocrystals and by the removal of the hole after excitation in III-V and II-VI nanocrystals.[14,43,44]

[1] S. Coe, W. K. Woo, M. Bawendi, and V. Bulovic, Nature (London) **420**, 800 (2002).
[2] A. J. Nozik, Annu. Rev. Phys. Chem. **52**, 193 (2001).
[3] A. P. Alivisatos, Nat. Biotechnol. **22**, 47 (2004).
[4] V. I. Klimov, J. Phys. Chem. B **110**, 16827 (2006).
[5] V. I. Klimov and D. W. McBranch, Phys. Rev. Lett. **80**, 4028 (1998).
[6] P. Guyot-Sionnest, M. Shim, C. Matranga, and M. Hines, Phys. Rev. B **60**, R2181 (1999).
[7] V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Phys. Rev. B **61**, R13349 (2000).
[8] B. L. Wehrenberg, C. Wang, and P. Guyot-Sionnest, J. Phys. Chem. B **106**, 10634 (2002).
[9] J. M. Harbold, H. Du, T. D. Krauss, K. S. Cho, C. B. Murray, and F. W. Wise, Phys. Rev. B **72**, 195312 (2005).
[10] U. Bockelmann and T. Egeler, Phys. Rev. B **46**, 15574 (1992).
[11] A. L. Efros, V. A. Kharchenko, and M. Rosen, Solid State Commun. **93**, 281 (1995).
[12] G. A. Narvaez, G. Bester, and A. Zunger, Phys. Rev. B **74**, 075403 (2006).
[13] P. Guyot-Sionnest, B. Wehrenberg, and D. Yu, J. Chem. Phys. **123**, 074709 (2005).
[14] A. Pandey and P. Guyot-Sionnest, Science **322**, 929 (2008).
[15] R. D. Schaller and V. I. Klimov, Phys. Rev. Lett. **92**, 186601 (2004).
[16] R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A. J. Nozik, A. Shabaev, and A. L. Efros, Nano Lett. **5**, 865 (2005).
[17] R. D. Schaller, V. M. Agranovitch, and V. I. Klimov, Nat. Phys. **1**, 189 (2005).
[18] S. J. Kim, W. J. Kim, Y. Sahoo, A. N. Cartwright, and P. N. Prasad, Appl. Phys. Lett. **92**, 031107 (2008).
[19] R. D. Schaller, M. A. Petruska, and V. I. Klimov, Appl. Phys. Lett. **87**, 253102 (2005).
[20] R. D. Schaller, M. Sykora, S. Jeong, and V. I. Klimov, J. Phys. Chem. B **110**, 25332 (2006).
[21] J. J. H. Pijpers, E. Hendry, M. T. W. Milder, R. Fanciulli, J. Savolainen, J. L. Herek, D. Vanmaekelbergh, S. Ruhman, D. Mocatta, D. Oron, A. Aharoni, U. Banin, and M. Bonn, J. Phys. Chem. C **111**, 4146 (2007); **112**, 4783 (2008).
[22] R. D. Schaller, J. M. Pietryga, and V. I. Klimov, Nano Lett. **7**, 3469 (2007).
[23] M. C. Beard, K. P. Knutsen, P. Yu, J. M. Luther, Q. Song, W. K. Metzger, R. J. Ellingson, and A. J. Nozik, Nano Lett. **7**, 2506 (2007).
[24] G. Nair and M. G. Bawendi, Phys. Rev. B **76**, 081304(R) (2007).
[25] M. Ben-Lulu, D. Mocatta, M. Bonn, U. Banin, and S. Ruhman, Nano Lett. **8**, 1207 (2008).
[26] M. T. Trinh, A. J. Houtepen, J. M. Schins, T. Hanrath, J. Piris, W. Knulst, A. P. L. M. Goossens, and L. D. A. Siebbeles, Nano Lett. **8**, 1713 (2008).
[27] J. A. McGuire, J. Joo, J. M. Pietryga, R. D. Schaller, and V. I. Klimov, Acc. Chem. Res. **41**, 1810 (2008).
[28] G. Allan and C. Delerue, Phys. Rev. B **73**, 205423 (2006).
[29] G. Allan and C. Delerue, Phys. Rev. B **77**, 125340 (2008).
[30] A. Franceschetti, J. M. An, and A. Zunger, Nano Lett. **6**, 2191 (2006).
[31] C. Sevik and C. Bulutay, Phys. Rev. B **77**, 125414 (2008).
[32] M. G. Bawendi, P. J. Carroll, W. L. Wilson, and L. E. Brus, J. Chem. Phys. **96**, 946 (1992).
[33] D. F. Underwood, T. Kippeny, and S. Rosenthal, J. Phys. Chem. B **105**, 436 (2001).
[34] G. Kalyuzhny and R. W. Murray, J. Phys. Chem. B **109**, 7012 (2005).
[35] E. Lifshitz, A. Glozman, I. D. Livitin, and H. Porteanu, J. Phys. Chem. B **104**, 10449 (2000).
[36] N. Myung, Y. Bae, and A. J. Bard, Nano Lett. **3**, 1053 (2003).
[37] S. Pokrant and K. B. Whaley, Eur. Phys. J. D **6**, 255 (1999).
[38] P. A. Frantsuzov and R. A. Marcus, Phys. Rev. B **72**, 155321 (2005).
[39] Y. M. Niquet, C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **62**, 5109 (2000).
[40] C. Delerue and M. Lannoo, *Nanostructures—Theory and Modeling* (Springer-Verlag, Berlin, 2004).
[41] L. Jdira, K. Overgaag, R. Stiufiuc, B. Grandidier, C. Delerue, S. Speller, and D. Vanmaekelbergh, Phys. Rev. B **77**, 205308 (2008).
[42] T. Okuno, Y. Masumoto, M. Ikezawa, T. Ogawa, and A. A. Lipovskii, Appl. Phys. Lett. **77**, 504 (2000).
[43] B. Mahler, P. Spinicelli, S. Buil, X. Quelin, J.-P. Hermier, and B. Dubertret, Nature Mater. **7**, 659 (2008).
[44] Y. Chen, J. Vela, H. Htoon, J. L. Casson, D. J. Werder, D. A. Bussian, V. I. Klimov, and J. A. Hollingsworth, J. Am. Chem. Soc. **130**, 5026 (2008).
[45] C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **48**, 11024 (1993).
[46] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1999).