phys. stat. sol. (c) **0**, No. 4, 1229–1232 (2003) / **DOI** 10.1002/pssc.200303100

Experimental and theoretical investigation of electronic structure in colloidal indium phosphide quantum dots

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Received 30 September 2002, accepted 2 December 2002
Published online 27 June 2003

PACS 81.07.Ta

We present detailed electronic structure calculations, based on an atomistic pseudopotential approach, for a 42 Å InP QD; theoretical results are correlated to results of experimental measurements. To better understand energy loss dynamics and mechanisms for hot carriers in QDs, we investigate relaxation between electronic levels in InP QDs with diameters significantly smaller than twice the Bohr exciton radius. Energy level spacings exceeding the optical phonon energy present the opportunity for slowed charge carrier cooling (phonon bottleneck effect). However, interaction between confined electrons and holes provides an alternate, efficient relaxation route. Therefore, we expect sufficiently fast charge separation to weaken the Coulomb interaction and decrease the electronic energy loss rate. We study electronic relaxation in InP QDs using variations of subpicosecond transient absorption spectroscopy.

1 Introduction Nanomaterials exhibit unique physical and chemical properties, and offer the potential to enhance the efficiency of solar energy conversion through utilization of hot carriers to either increase the photovoltage or to increase the photocurrent via impact ionization [1]. Colloidally-prepared semiconductor QDs lie typically in the 10 Å to 100 Å diameter range, and display clear quantum size effects, including emission blue-shifted from that of the bulk, and absorption spectra which include discrete exciton transition features. The large spacings between conduction levels of many tens of meV or more have been the subject of carrier relaxation studies seeking evidence for or against the phonon bottleneck effect. The phonon bottleneck effect [2–4] in colloidal QDs has proven elusive; electron-hole carrier-carrier scattering has been shown to yield an efficient energy relaxation channel for hot electrons [5, 6]. Charge separation on a timescale competitive with relaxation offers the best route to slowed electronic relaxation. We discuss here results based on theoretical and experimental investigations of electronic structure and relaxation in InP QDs. We identify single particle levels and exciton states for a 42 Å diameter InP QD, including states with orbital angular momentum of S, P, and D symmetry. Our experimental results based on transient absorption (TA) spectroscopy yield spectral data in good agreement with theoretical electronic structure calculations, and our time-dependent data indicate that fast charge carrier separation leads to slowed relaxation of hot electrons.

2 Theoretical To determine the electronic structure in more detail than previously available, as well as to compare experiment with theory, we calculated excitonic energies for a 41.8 Å diameter InP QD using the atomistic pseudopotential method [7]. Initially we compute 32 single-particle valence states and 16

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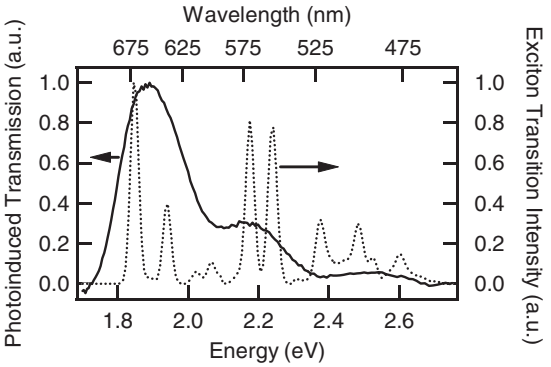

Fig. 1 Theoretical excitonic spectrum (dotted line) for a sample of 41.8 Å diameter InP quantum dots. The transition intensity is proportional to the absorption coefficient, and consists of a sum of the oscillator strengths for various excitonic transitions. The solid line shows the measured photoinduced bleach spectrum, at a delay of 1.0 ps following photoexcitation at 3.2 eV, for a sample with average size of ~42 Å diameter.

single-particle conduction states by solving the Schrödinger equation. Next, we calculated the excitonic energy levels and wavefunctions using the configuration interaction (CI) [8] approach, including the Coulomb interaction energy. The theoretical transition spectrum obtained from our CI calculation is illustrated in Fig. 1, revealing seven major peaks. The peak at 1.84 eV arises from the transition between the two highest-energy s-like valence states and the lowest s-like conduction state. The peak at 1.94 eV comes from the transition between the split-off s-like valence state and the lowest conduction state. The two peaks at 2.18 and 2.24 eV are attributed to the transitions from p-like valence states to p-like conduction states. Calculated peaks from 2.3 to 2.7 eV are mainly due to the d-like single-particle states. Comparing the experimental spectrum with that predicted by theory shows that each of the broad experimental peaks at ~1.9 eV or ~2.15 eV actually result from two distinct transitions. Similarly, the broad experimental peak at ~2.5 eV results from three exciton transitions. Calculations with this level of detail and including the higher conduction states have not yet been carried out on other dot sizes.

3 Experimental procedure Indium phosphide QDs were synthesized using standard colloidal methods, in the presence of trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP), as previously reported [9]. Our samples consist of colloidal suspensions of InP QDs, either as-prepared or n-type. As prepared, the dots are capped with TOP/TOPO and suspended in hexane. The n-type QDs are prepared as previously described [10]: briefly, sodium biphenyl is added to QDs suspended in heptamethylnonane, and the biphenyl anion chemically injects electrons into the conduction band of the QDs. The mean diameter of InP QDs studied here have been determined by the energy of their first exciton absorption [11], and typically exhibit a size distribution of ±5% to ±10%. Measurements have been conducted at room temperature on colloidal QD solutions contained in a demountable liquid cell with sapphire windows. The optical density is adjusted to O.D. ~0.1 at the first exciton energy.

Transient absorption measurements are made on both as-prepared (TOP, TOPO capped) InP QDs as well as n-type InP QDs. Thus we have the ability to measure relaxation rates, following visible and/or infrared pump, of either neutral dots (photoexcited excitons) or charged dots (chemically injected electrons, no visible excitation pulse required). Our transient absorption experimental setup has been described previously [12]. Measurements consist of (a) visible pump with white light (WL) probe, (b) visi-

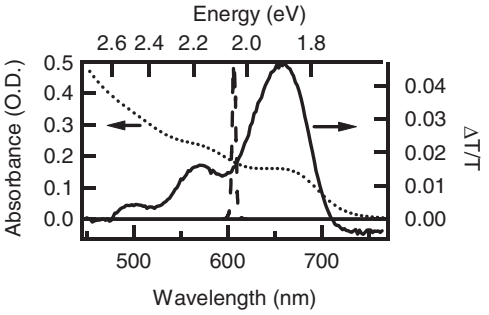

Fig. 2 Linear (dotted line) and transient (solid line) absorption spectra for 43 Å InP QDs; for transient measurement, excitation at 3.2 eV, t_{pr} = 500 fs. Dashed line shows the excitation pulse used in the three-pulse experiment. Three distinct transitions are evident: 1S (1.89 eV); 1P (2.17 eV); and 1D (2.49 eV).

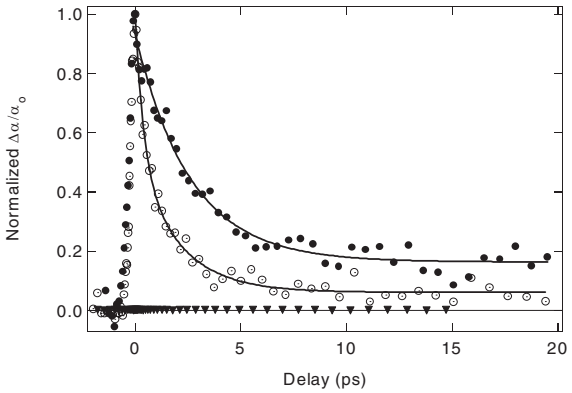

Fig. 3 Transient absorption traces comparing dynamics of S bleach recovery in 50 Å InP QDs. Open circles show neutral QDs where the S exciton is created via visible pump in the three pulse experiment. Closed circles show n-type QDs where S electron injected chemically and pumped only with IR pulse. Triangles show neutral QDs pumped only with IR pulse.

ble and infrared pumps with (WL) probe (three pulse measurement), or (c) infrared pump with WL probe. Figure 2 shows the linear and transient absorption spectra for a sample of 43 Å diameter QDs. A three pulse measurement typically involves excitation just above the first exciton energy, followed by a delayed (t_{IR}) infrared pulse to boost the exciton from S to P. These variations of TA spectroscopy allow us to measure the spectral and temporal dependence of the photoinduced change in absorption by (a) photoexciting at or above the first exciton transition and probing with the WL, (b) photoexciting across the band gap, then photoexciting with an infrared pulse tuned to the S-P transition energy, or (c) photoexciting chemically-injected electrons from the S to the P conduction levels [10]. Measurements are typically made exciting at an average per-dot exciton density $\langle N_0 \rangle \leq 0.5$ electron–hole pairs per dot, which simplifies experimental interpretation by largely avoiding multi-pair Auger recombination effects [13].

4 Experimental results and discussion Our experimental investigations of colloidal InP QDs indicate that while correlated electron–hole pairs confined to the dot core, i.e. excitons, yield fast energy loss (cooling) rates, electrons in the absence of holes cool more slowly. We commonly measure TA spectra (fixed delay) and dynamics (fixed probe energy) on colloidal QDs by photoexciting in the visible above

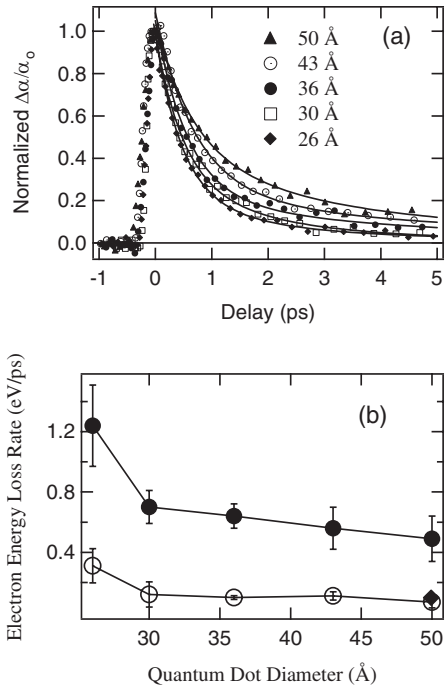

Fig. 4 a) Normalized recovery of S bleaching in three-pulse experiment for five InP QD samples with different mean diameters. Symbols are data and solid lines are bi-exponential fits. b) Exciton energy loss rate as a function of QD diameter. Calculated using average values for bi-exponential fit and energy spacing between S and P transition. Slow component is shown as open circles and fast component shown as closed circles. Also shown as the filled diamond is the energy loss rate for CB electron in n-type 50 Å QDs.

the first exciton state and probing at the energy of the S exciton peak. Analysis of such a measurement is complicated by the contribution of the carrier-induced Stark effect to the TA signal. We therefore utilize an approach consisting of photoexcitation just slightly above the S exciton transition and then, after a variable delay, photoexciting again with an infrared pulse for which the photon energy is tuned to the difference between the S and P exciton peaks. As shown in Fig. 3 (open circles), when probing the dynamics at the S exciton energy, we consistently observe two relaxation components of approximately 400 fs and 3 ps. We attribute the two characteristic times to two classes of QDs within our sample: those QDs which exhibit surface hole traps yield a slower relaxation due to fast charge separation of the hole to the surface trap, and those QDs without any surface hole trap yield faster relaxation owing to a stronger Coulomb coupling which permits relaxation through the more closely spaced excitonic states. We investigate the possibility of slowed electron relaxation in InP QDs by measuring the infrared pump, WL probe of n-type dots. The recovery dynamics, measured at the first exciton energy following excitation of chemically injected electrons with an infrared pump tuned to the spacing between the two lowest conduction levels, indicate a single exponential with lifetime in the 2–4 ps range (filled circles, Fig. 3). Thus, relaxation for the electron in the absence of the hole appears to validate the explanation that Coulomb interaction speeds up by a factor of ten the electronic relaxation time for an exciton vs. an electron in the absence of a hole.

As the dot size decreases, the gap between the S and P exciton peaks increases; we have investigated the dynamics of electron relaxation between the P and S exciton states for QDs of various sizes, and find no evidence of the phonon bottleneck (Fig. 4a). Fig. 4b shows the size dependence of the average rate of energy loss for relaxation from the P to S exciton states, as well as the energy loss rate for the 50 Å diameter n-type QDs.

5 Conclusions Excitonic structure calculations indicate that experimentally measured transient absorption spectra do not resolve all exciton transitions. The excitonic structure consists of levels, both orbitally allowed and forbidden, which create a relatively dense manifold through which relaxation can proceed. Our transient absorption measurements on colloidal InP QDs indicate that electronic relaxation for core-confined excitons proceeds much more quickly than for a core-confined electron whose Coulomb interaction with a hole or other positively charged species is weak: we observe a five- to ten-fold longer relaxation time for electrons than for excitons. Further research to determine the temperature dependence and mechanism for relaxation of hot electrons in the absence of holes is underway.

Acknowledgements The authors from the National Renewable Energy Laboratory wish to thank the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences for generous financial support. H. Fu thanks the NSF for financial support (DMR-0116315).

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