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Spectral hole burning and zero phonon linewidth in semiconductor nanocrystals

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Spectral hole burning reveals a sharp zero-phonon line (ZPL) as well as discrete acoustic phonon sidebands in CdSe nanocrystals. The ZPL linewidth obtained from the spectral hole burning depends strongly on the measurement time scale, reflecting effects of spectral diffusion. The nonlinear optical measurement allows us to suppress effects of spectral diffusion leading to a ZPL linewidth as narrow as 6 μeV.

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Semiconductor nanocrystals are characterized by discrete electronic energy levels and also by the presence of discrete acoustic phonon modes. The optical absorption spectrum of a semiconductor nanocrystal is therefore expected to feature a zero-phonon line (ZPL) involving no absorption or emission of phonons as well as discrete optical and acoustic phonon sidebands arising from transitions assisted by absorption or emission of optical and acoustic phonons. The linewidth of the ZPL sets the intrinsic limit for decoherence and thus is of particular importance for potential applications such as quantum information processing.[1,2]

A major difficulty in probing optical properties of semiconductor nanocrystals is spectral diffusion, i.e., random spectral shifts in the optical transition frequency due to fluctuations in the microscopic local environment. In the presence of spectral diffusion, the measured linewidth of the ZPL becomes dependent on the measurement time scale.[3] Previous photoluminescence (PL) studies of single nanocrystals have shown an upper limit of 120 μeV for ZPL linewidth in CdSe nanocrystals at low temperature.[3] Quantitatively similar results have also been obtained in accumulated photon echo studies in a collection of inhomogeneously broadened CdSe nanocrystals.[4] For both of these studies, the measurement time scale far exceeds time scales at which spectral diffusion occurs. In comparison, ZPL linewidths of only a few μeV have been observed in photon echo studies of self-assembled $In_xGa_{1-x}As$ quantum dots (QD's) grown by molecular beam epitaxy.[5]

In this Rapid Communication we report studies of absorption spectra of CdSe/ZnS core/shell nanocrystals using techniques based on spectral hole burning (SHB). The SHB response exhibits a sharp resonance due to the ZPL and clearly resolved sidebands due to confined acoustic phonons. The ZPL linewidth obtained from SHB depends strongly on the measurement time scale. This along with additional studies using frequency-domain four-wave mixing (FWM) elucidates how these ensemble nonlinear optical measurements can be sensitive to and can be used to probe spectral diffusion. Using modulation frequencies as high as a few MHz to suppress effects of spectral diffusion in SHB, we have obtained ZPL linewidth as small as 6 μeV.

High quality ZnS-capped CdSe nanocrystals used in our study were fabricated with high temperature organometallic synthesis.[6] The nanocrystals were characterized by absorption, PL, transmission electron micrograph (TEM), and time-resolved PL.[7] Average core diameters were determined from PL spectra and are consistent with results of TEM. The nanocrystals were dispersed in a thin film of polystyrene deposited on a sapphire disk.

For measurements at low temperature, the sample was mounted in a helium flow cryostat. Two tunable dye lasers (Coherent-899), each frequency-stabilized to their respective external reference cavity, were used in SHB and FWM studies. Tunable diode lasers (New Focus) were also used for the tuning range between 632 and 638 nm. The laser linewidth is narrower than 0.01 μeV (2.5 MHz). These lasers allowed us to investigate CdSe nanocrystals with an average core diameter D ranging from 4 to 9 nm. For SHB studies, the change in the transmission of a probe beam induced by a pump beam was measured using lock-in detection. The intensity of the pump beam was modulated with an acousto-optic modulator.

Figures 1(a) and 1(b) show the differential transmission spectrum obtained at $T=10$ K for nanocrystals with $D=9$ and 4 nm, respectively. The nonlinear response was measured as a function of the detuning between the pump and the probe field. In order to probe the lowest energy dipole optical

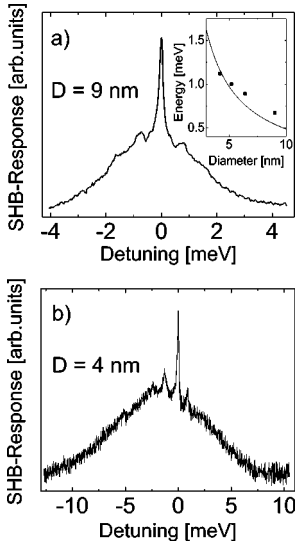

FIG. 1. SHB response obtained at $T=10$ K and $\Omega=20$ kHz ($I_{pump}=1$ W/cm^2). (a) $D=9$ nm. (b) $D=4$ nm. The inset shows the size dependence of the energy separation between the ZPL and the first sideband. The solid line is the calculated energy for confined acoustic phonons with $l=2$ and $n=1$.

transition, the frequency of the pump was fixed at the lower energy part of the inhomogeneous absorption profile of the $1S_e1S_{h,3/2}$ transition of the respective sample ($\lambda_{\text{pump}}=635$ and 565 nm for $D=9$ and 4 nm, respectively). Similar results were also obtained near or above the absorption line center (no SHB response could be obtained outside the inhomogeneous absorption profile). SHB responses shown in Fig. 1 feature a sharp resonance at zero pump-probe detuning, well-resolved sidebands, and a much broader pedestal.[8]

We first discuss the sidebands and the pedestal. In the SHB measurement, the pump and probe can couple to different transitions in the manifold of zero-phonon and phonon-assisted optical transitions, giving rise to the sidebands and the broad pedestal in the SHB response. The spectral range of acoustic phonons that can couple to the optical transition determines the linewidth of the acoustic phonon pedestal (and also the initial rapid decay in photon echo studies[4,5]). The measured linewidth as well as its size dependence agree well with the theoretical expectation.[9,10] The well-resolved sidebands are due to confined acoustic phonon modes that have a relatively long lifetime and can couple strongly to the optical transition. These sidebands arise when one beam couples to the ZPL while the other couples to the phonon-assisted transition. The inset of Fig. 1(a) plots the phonon energy obtained from the first sideband in the SHB response as a function of D. Also shown in the figure is the calculated size dependence of the phonon energy for the confined acoustic phonon mode with $l=2$, $n=1$ where l and n are angular momentum and radial mode numbers, respectively. A spherical shape for the nanocrystals is assumed in the theoretical model.[11] We attribute the discrepancy between theory and experiment for large nanocrystals to the fact that the shape of the nanocrystals becomes increasingly prolate with increasing size, as can be seen from TEM. While confined acoustic phonons have been observed in earlier studies,[11–13] the SHB response elucidates directly the role of these phonons in the optical transition.

We now turn to the SHB resonance at zero detuning. The SHB response at or near zero detuning arises when the pump and probe couple to the same optical transition. The sharp resonance at zero detuning is due to the ZPL. With increasing nanocrystal size, the ZPL becomes more pronounced relative to the phonon pedestal due to decreasing electron-phonon coupling. The ZPL vanishes at temperatures above 40 K (not shown).

In the limit of the third order nonlinear optical response, the linewidth of the SHB resonance is given by twice the homogeneous linewidth. This is no longer true, however, in the presence of spectral diffusion, i.e., if the optical transition frequency fluctuates as a function of time, since the SHB linewidth now becomes dependent on the time scale of the measurement. For SHB using lock-in detection, the measurement time scale is set by the modulation period in the pump intensity. In the limit that the modulation period is long compared with the time scale at which spectral diffusion takes place, spectral diffusion can lead to significant broadening of the SHB resonance. Figure 2(a) shows the linewidth [full width at half maximum (FWHM)] of the SHB resonance as a function of the modulation frequency Ω. The inset shows the same data with a logarithmic scale for Ω. The SHB linewidth decreases rapidly as the modulation frequency is increased from 1 kHz to a few hundred kHz, indicating that effects of spectral diffusion are most pronounced at these time scales. The SHB linewidth obtained at modulation frequencies of a few MHz approaches an asymptotic value, as shown in Fig. 2(a). More insight into the Ω dependence will be provided in discussions on the lifetime of the excitations causing the SHB response.

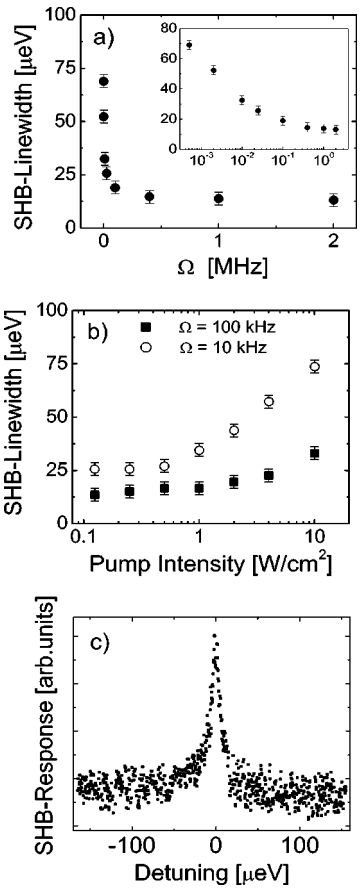

FIG. 2. (a) Modulation frequency dependence of the SHB linewidth ($I_{\text{pump}}=I_{\text{probe}}=0.5$ W/cm^2). The inset shows the same data, however, with a logarithmic scale for the modulation frequency. (b) Intensity dependence of the SHB linewidth with $I_{\text{probe}}=0.5$ W/cm^2. (c) An expanded scan of the SHB resonance obtained at $\Omega=1$ MHz with $I_{\text{pump}}=2I_{\text{probe}}=1$ W/cm^2. All data were obtained at $T=2$ K and for nanocrystals with $D=9$ nm.

The SHB linewidth also depends strongly on the level of optical excitation. Figure 2(b) shows the linewidth of the SHB resonance as a function of the pump intensity obtained at $\Omega=10$ and 100 kHz. The linewidth broadens significantly with increasing pump intensity. This power broadening can result from saturation beyond the third-order limit and can also result from intensity-dependent spectral diffusion processes. Although SHB is a nonlinear measurement, the pump intensity (≈ 0.5 W/cm^2) used for Fig. 2(a), at which the SHB linewidth is nearly independent of the excitation level, is considerably lower than typical intensities used for single-nanocrystal PL studies (≈ 10 W/cm^2 or greater).

Figure 2(c) is an example of an expanded scan of the SHB

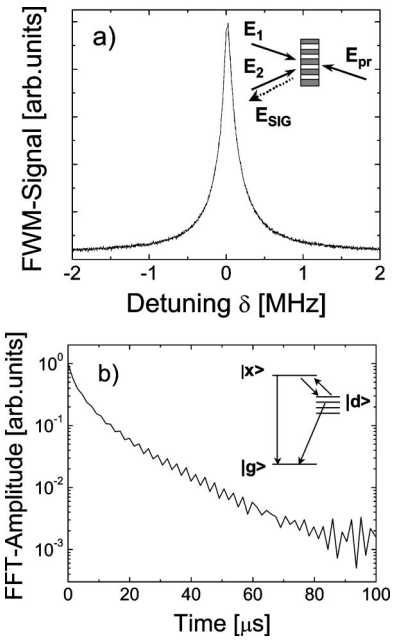

FIG. 3. (a) FWM response obtained at $T=10$ K ($I_1=I_2=I_{\rm pr}=1$ W/cm^2). The inset shows the FWM geometry. (b) Fourier transform of the FWM response exhibiting nonexponential decay. The inset shows the energy level structure discussed in the text.

resonance obtained at $\Omega=1$ MHz. The SHB resonance corresponds to a ZPL linewidth (FWHM) of 6 μeV. All the data in Fig. 2 were obtained for nanocrystals with $D=9$ nm. Qualitatively the same behavior has also been observed for nanocrystals with D ranging from 4 to 9 nm. In particular, the ZPL linewidth obtained in the asymptotic limit of large Ω and low excitation levels does not show a significant size dependence within the size range investigated. Note that along with a pronounced decrease in the linewidth, the SHB signal also decreased nearly two orders of magnitude as we increased Ω from 1 kHz to 1 MHz. The deteriorating signal-to-noise ratio has prevented us from increasing Ω to significantly above a few MHz. This also indicates that the physical mechanism underlying the SHB response features a relatively long lifetime.

To determine the lifetime and especially the physical mechanism of the SHB response, we have carried out additional studies employing nearly degenerate frequency-domain FWM.[14,15] These studies are based on the use of two pump beams instead of only one pump beam. As shown in the inset of Fig. 3(a), two pump fields E_1 and E_2 with frequencies ω_1 and ω_2 interact in the sample and induce a population grating that oscillates at a frequency of $\delta=|\omega_1-\omega_2|$. The oscillating population grating can form if the detuning δ is small compared with the decay rate of the grating. A probe field $E_{\rm pr}$, with frequency $\omega_{\rm pr}$ and counterpropagating with respect to E_1, scatters off the grating and generates a FWM signal with frequency $\omega_s=\omega_1+\omega_{\rm pr}-\omega_2$ along the direction counterpropagating with respect to E_2. This FWM response can be understood as SHB induced by the population grating. FWM responses as a function of detuning δ (with $\omega_1=\omega_{\rm pr}$ fixed) can provide information on the decay of the population grating. Figure 3(a) shows such a response obtained at 10 K and for nanocrystals with $D=9$ nm. The FWM lineshape is non-Lorentzian, which is also clearly shown by the highly nonexponential Fourier transform of the spectral response [Fig. 3(b)].

The time scales observed in the above FWM study are several orders of magnitude longer than the radiative lifetime ($\approx$10 ns) for the relevant dipole optical transition,[7] indicating that the FWM as well as the SHB response is due to depletion of the ground state ($|g\rangle$) rather than population of the dipole-allowed exciton states ($|x\rangle$). To illustrate this, we consider an energy level system shown schematically in the inset of Fig. 3(b). For this system, excitons, generated resonantly by the pump, can decay or dissociate into states $|d\rangle$, for which rapid radiative recombination is not allowed. Since saturation of the dipole optical transition is determined by $(\rho_{xx}-\rho_{gg})$, the population difference between $|x\rangle$ and $|g\rangle$, the nonlinearity can arise by populating $|x\rangle$ and/or by depleting the population in $|g\rangle$. The depletion occurs when the excitation is prevented from returning to $|g\rangle$. In this regard, keeping nanocrystals in $|d\rangle$ induces a nonlinear optical response. The lifetime associated with this response is determined by the time it takes for nanocrystals in $|d\rangle$ to recover to $|x\rangle$ or $|g\rangle$. In comparison, the lifetime associated with the nonlinear response due to population in $|x\rangle$ is determined by the lifetime of $|x\rangle$. The FWM response shown in Fig. 3(a) features relatively slow time scales and thus is primarily due to nanocrystals in $|d\rangle$, with negligible contributions from nanocrystals in $|x\rangle$. This is not surprising since the lifetime of $|d\rangle$ is much longer than the lifetime of $|x\rangle$. On average excited nanocrystals spend much longer time in $|d\rangle$ than in $|x\rangle$.

Using optical Bloch equations and the energy levels shown in the inset of Fig. 3(b) and assuming nanocrystals are inhomogeneously broadened, we have calculated the third order nonlinear optical polarization for the FWM response due to nanocrystals in $|d\rangle$ (effects of spectral diffusion are not included):

$$P^{(3)}\propto\mu^4\frac{E_1E_2^*E_{\rm pr}e^{-i\omega_s t}}{(\delta+i\Gamma_d)(\delta+i\Gamma_x)(\omega_s-\omega_2+2i\gamma)}+\text{c.c.}, \quad (1)$$

where μ and γ are the matrix element and intrinsic decoherence rate for the $|g\rangle-|x\rangle$ transition, respectively, and Γ_x and Γ_d is the population decay rate for $|x\rangle$ and the recovery rate for nanocrystals in $|d\rangle$, respectively. In the limit that $\Gamma_d \ll \Gamma_x$, FWM response as a function of δ is then characterized by a Lorentzian with a width of $2\Gamma_d$. Equation (1) has only used a single state for $|d\rangle$. For a distribution of $|d\rangle$ along with a distribution of Γ_d and possible relaxation among states in $|d\rangle$, one then expects a non-Lorentzian FWM spectral lineshape, consistent with the experimental results shown in Fig. 3.

The above model is motivated by extensive studies of PL intermittency in semiconductor nanocrystals.[3,16] While the underlying microscopic details still remain unclear, it is believed that photoexcited carriers can be trapped at the surface of a nanocrystal with a distribution of trapping depths, leading to a power-law distribution for the ''off'' time in the intermittency.[16] It should be pointed out that for the nonlin-

ear optical measurement, intrinsic dipole-forbidden exciton states in the fine structure of the $1S_e1S_{h,3/2}$ transition should be included in $|d\rangle$ instead of $|x\rangle$, since resonant optical excitation of these transitions is negligible compared with that of resonant dipole optical transitions.

The process of PL intermittency is strongly correlated with spectral diffusion.[17] As a nanocrystal cycles through its ''off'' and ''on'' states, the particular charge configuration on the nanocrystal surface changes, leading to fluctuating internal electric fields and hence to fluctuating optical transition frequencies. SHB measures the distribution in the relevant dipole optical transition frequency of nanocrystals in $|d\rangle$. For these nanocrystals, the transition frequency before the optical excitation is at the frequency of the pump laser. Performing the SHB measurement at a given Ω eliminates contributions from those nanocrystals for which the recovery time is much longer than the modulation period. Effects of spectral diffusion occurring in these nanocrystals are thus suppressed or eliminated from the measurement. A comparison of the relevant time scales in SHB and FWM measurements in Fig. 2(a) and Fig. 3(a) further confirms this correlation between the nanocrystal recovery time and the effects of spectral diffusion on SHB linewidth. The correlation discussed above also points to an interpretation for the observation that the SHB linewidth approaches an asymptotic value at Ω of a few MHz [see Fig. 2(a)]. If the recovery lifetimes for trapped carriers are long compared with the lifetime of the lowest energy dipole forbidden exciton state (≈ 1 μs),[18] the SHB response obtained at Ω of a few MHz should then be primarily due to nanocrystals in the intrinsic dark exciton state. In the absence of rapid spectral diffusion for these excitons, the SHB linewidth should then approach an asymptotic value determined by the intrinsic linewidth for the ZPL. Note that the SHB linewidth obtained at high modulation frequencies ($\Omega > 1$ MHz) is comparable to that obtained in self-assembled $In_xGa_{1-x}As$ QD's.[5]

In summary, we have shown that SHB responses in CdSe nanocrystals feature pronounced ZPL as well as discrete acoustic phonon sidebands. The SHB response arises from nanocrystals that remain in dark or nonemitting states and provide an effective probe for the underlying spectral diffusion processes. By suppressing effects of spectral diffusion in the nonlinear measurement, we have obtained an upper bound of 6 μeV for the ZPL linewidth, over one order of magnitude smaller than that reported in previous studies, suggesting the potential of these nanocrystals for applications such as quantum information processing. A main challenge, however, is to further improve surface properties of semiconductor nanocrystals such that carrier trapping and rapid spectral diffusion processes can be eliminated or significantly reduced.

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[1] K.R. Brown, D.A. Lidar, and K.B. Whaley, Phys. Rev. A **65**, 012307 (2002).
[2] T.A. Brun and H. Wang, Phys. Rev. A **61**, 032307 (2000).
[3] For recent review, see S.A. Empdocles, R. Neuhauser, K. Shimizu, and M.G. Bawendi, Adv. Mater. (Weinheim, Ger.) **11**, 1243 (1999).
[4] K. Takemoto, B.R. Hyun, and Y. Masumoto, Solid State Commun. **114**, 521 (2000); Y. Masumoto, T. Kawazoe, and N. Matsuura, J. Lumin. **76**, 189 (1998).
[5] P. Borri, W. Langbein, S. Schneider, U. Woggon, R.L. Sellin, D. Ouyang, and D. Bimberg, Phys. Rev. Lett. **87**, 157401 (2001); D. Birkedal, K. Leosson, and J.M. Hvam, *ibid.* **87**, 227401 (2001).
[6] M.A. Hines and P. Guyot-Sionnest, J. Phys. Chem. **100**, 468 (1995).
[7] X. Fan, M.C. Lonergan, Y. Zhang, and H. Wang, Phys. Rev. B **64**, 115310 (2001).
[8] P. Palinginis and H. Wang, Appl. Phys. Lett. **78**, 1541 (2001).
[9] T. Takagahara, J. Lumin. **70**, 129 (1996).
[10] B. Krummheuer, V.M. Axt, and T. Kuhn, Phys. Rev. B **65**, 195313 (2002).
[11] L. Saviot, B. Champagnon, E. Duval, I.A. Kudriavtsev, and A.I. Ekimov, J. Non-Cryst. Solids **197**, 238 (1996).
[12] T.D. Krauss and F.W. Wise, Phys. Rev. Lett. **79**, 5102 (1997).
[13] U. Woggon, F. Gindele, O. Wind, and C. Klingshirn, Phys. Rev. B **54**, 1506 (1996).
[14] J.T. Remillard, H. Wang, M.D. Webb, and D.G. Steel, J. Opt. Soc. Am. B **7**, 897 (1990).
[15] H. Wang, M. Jiang, and D.G. Steel, Phys. Rev. Lett. **65**, 1255 (1990).
[16] M. Kuno, D.P. Fromm, H.F. Hamaan, A. Gallagher, and D.J. Nesbitt, J. Chem. Phys. **112**, 3117 (1999).
[17] R.G. Neuhauser, K.T. Shimizu, W.K. Woo, S.A. Empedocles, and M.G. Bawendi, Phys. Rev. Lett. **85**, 3301 (2000).
[18] M. Nirmal *et al.* Phys. Rev. Lett. **75**, 3728 (1995).