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Effect of glass electronic states on carrier dynamics in semiconductor quantum-dot structures

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Ultrafast carrier dynamics of $CdS_{0.4}Se_{0.6}$ nanocrystals excited at various photon energies are investigated by femtosecond nonlinear transmission spectroscopy. As the excitation photon energy is decreased, the enhanced bleaching and its rapid recovery of $1S(e)$-$1S_{3/2}(h)$ state are observed with the development of an additional $1S(e)$-$2S_{3/2}(h)$ bleaching and a spectrally broad photoinduced absorption. We have found that the electron trapping into the glass electronic states has significant effect on the carrier dynamics by reducing the carrier densities in both confined and surface states as the photoexcitation energy increases.

Semiconductor nanocrystals doped in glass matrices or prepared chemically in solutions have been a subject of increasing interest due to various unique physical properties.[1] Owing to the three-dimensional quantum confinement effect, the electronic states are significantly modified in semiconductor nanocrystals with dimensions smaller than the bulk exciton Bohr radius.[2–4] In combination with theoretical developments on the energy states of the nanocrystals considering image-charge effect,[3] finite confinement potential well,[5] Coulomb interaction,[6,7] valence-band mixing,[7,8] and nonparabolic conduction band,[8] the lowest energy state in nanocrystals has been investigated in detail. In addition, photoluminescence excitation (PLE) and nonlinear transmission techniques have been applied, where the inhomogeneous effect was avoided by exciting nanocrystals size selectively.[9] Norris and Bawendi have employed the PLE spectroscopy to elucidate the electronic states of CdSe quantum dots including $1S(e)$-$1S_{3/2}(h)$, $1S(e)$-$2S_{3/2}(h)$, $1P(e)$-$1P_{3/2}(h)$, and even other higher states.[10]

The large surface-to-volume ratio is also an important factor for determining various optical properties of nanocrystals. Many atoms locating at the boundary increase the number of dangling bonds to form the surface states. The surface states have been suggested as a possible deactivation channel for the fast carrier relaxation in the band-edge photoluminescence.[11] Moreover, it has been reported that the electrons are trapped into the glass electronic states, inducing photodarkening in nanocrystals.[12]

Recently, the ultrafast carrier dynamics in CdS, CdSe, and CdS_xSe_{1-x} nanocrystals have been investigated by using various femtosecond spectroscopic techniques. The fluorescence up-conversion experiment has revealed that the fast photoluminescence decay (~ 1 ps) in CdS nanocrystals is caused by trapping holes into negatively charged acceptors.[13] The femtosecond pump-probe study has indicated that even Auger-assisted hole trapping into surface/interface-related states possibly occurs in CdS nanocrystals photoexcited with high intensity.[14] Moreover, subpicosecond $1P$-to-$1S$ relaxation due to Auger-type electron-hole energy transfer was observed in CdSe nanocrystals instead of the reduced energy relaxation rate arising from the phonon bottleneck effect.[15]

In addition to the confined state bleaching of CdS_xSe_{1-x} nanocrystals, a broad photoinduced absorption has been observed below band gap.[16] The time-resolved differential transmission measurements of $CdS_{0.4}Se_{0.6}$ nanostructures have revealed that the buildup of the photoinduced absorption is accomplished within less than 1 ps.[17] In addition, the decay dynamics is strongly dependent on the excitation intensity. The photoinduced absorption has been suggested to originate from the reabsorption from surface traps to quasicontinuum states at the semiconductor-glass interfaces, where the quasicontinuum surface states have been proposed based on the strong electron-phonon coupling in nanocrystals.[18]

In the present paper, we report the effect of electron trapping into the glass electronic states on the carrier dynamics of $CdS_{0.4}Se_{0.6}$ nanocrystals by investigating the femtosecond nonlinear transmission spectra excited at various photon energies. As the excitation photon energy decreases, we have observed the unusually enhanced bleaching and its fast recovery of $1S(e)$-$1S_{3/2}(h)$ state with the appearance of an additional $1S(e)$-$2S_{3/2}(h)$ bleaching as well as a broad photoinduced absorption below the band gap. Our data indicate that, as the photoexcitation energy increases, the electron trapping into the glass electronic states affect significantly on the carrier dynamics by reducing the carrier densities in both confined and surface states.

The sample employed in our experiment is $CdS_{0.4}Se_{0.6}$ nanocrystals doped in a borosilicate glass matrix, which is a commercially available long-pass color filter from Schott Glass, Inc (RG630). The average radius $R = 3.7$ nm and the volume fraction $f_v = 3.2\times10^{-3}$ have been estimated by small angle neutron scattering method.[19] The inset of Fig. 1(a) shows the linear absorption (solid line) and the photoluminescence (dotted line) spectra. In the linear absorption spectrum, a resonant feature arising from the confined electron-hole pair states can be seen just above the absorption edge. The band-edge photoluminescence is slightly redshifted due to hole trapping.[13] The low-energy photolumines-

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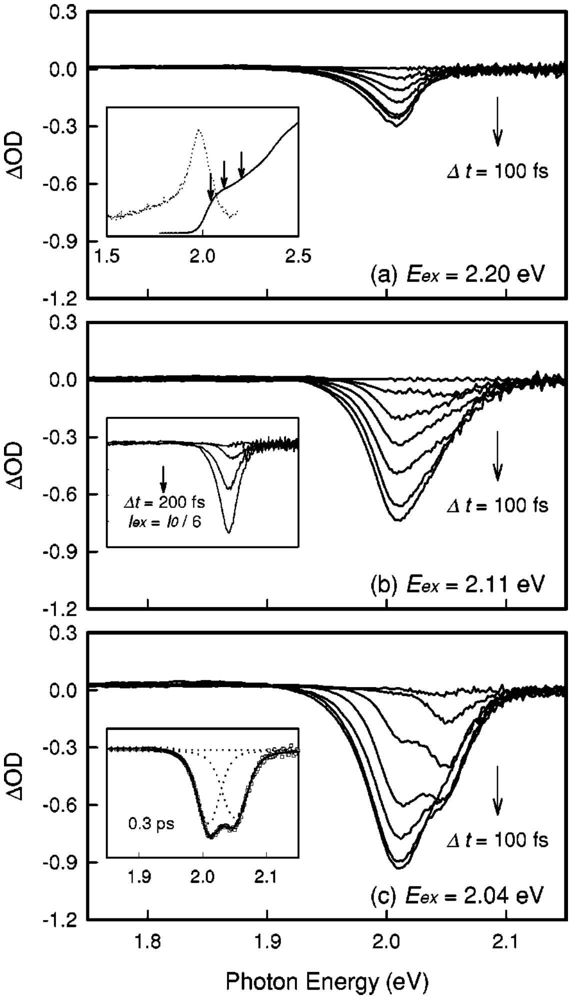

FIG. 1. The bleaching build up of the $1S(e)$-$1S_{3/2}(h)$ and $1S(e)$-$2S_{3/2}(h)$ states in the $CdS_{0.4}Se_{0.6}$ nanocrystals excited at (a) 2.20 (565), (b) 2.11 (590), and (c) 2.04 eV (610 nm). Inset to (a): linear absorption (solid) and cw PL (dotted) spectra. Inset to (b): bleaching spectra under low-intensity excitation. Inset to (c): bleaching spectrum observed at 0.3 ps with two composite Voigt profiles at 2.01 and 2.05 eV.

cence, tailing off below 1.5 eV, is mainly attributed to the recombination from the deep traps to the impurity levels near the valence band or to the ground state.[11]

In the transient absorption measurements, the nanocrystals are excited by femtosecond laser pulses at 2.20 (565), 2.11 (590), and 2.04 eV (610 nm). The excitation photon energies are chosen to be slightly above the $1S(e)$-$1S_{3/2}(h)$ state and far below the $1P(e)$-$1P_{3/2}(h)$ state. The excitation pulses are generated by frequency-doubling of the infrared-optical parametric amplifier output, which is pumped by a regeneratively amplified mode-locked Ti-sapphire laser (800 nm, 100 fs, and 1 kHz). The excited carrier density is kept constant by adjusting energy density between 0.1 and 0.2 mJ/cm^2 to compensate the different optical density at each excitation photon energy. The possible self-saturation effect is assumed to be almost the same because of small variation of energy density. The absorption change after photoexcitation is probed by the delayed femtosecond continuum pulses generated in water and is recorded by a 0.15-m imaging spectrograph equipped with a cooled dual diode array. The absorption change is measured in ΔOD, which is defined by the difference in the optical densities (OD's) between the presence and the absence of the pump pulses.

Figures 1(a)–1(c) show the transient absorption spectra at 100 fs delay intervals in the build-up regime. The photoexcitation energies of 2.20 (565), 2.11 (590), and 2.04 eV (610 nm) are indicated by the arrows on the absorption spectrum in the inset of Fig. 1(a). In case of 2.20 eV excitation [Fig. 1(a)], only the $1S(e)$-$1S_{3/2}(h)$ bleaching band is observed at 2.01 eV over the entire spectral region. As the excitation energy is changed into 2.11 eV [Fig. 1(b)], however, the unique enhancement of the bleaching is observed along with the development of the weak $1S(e)$-$2S_{3/2}(h)$ bleaching at 2.05 eV. Since the bleaching band disappears at low pumping intensity [inset of Fig. 1(b)], we can conclude that the growth of the $1S(e)$-$2S_{3/2}(h)$ bleaching is not originated from the resonance with photoexcitation energy but from the high-carrier density. Finally, as the nanocrystals are excited at 2.04 eV [Fig. 1(c)], the $1S(e)$-$2S_{3/2}(h)$ bleaching state becomes remarkably enhanced so that the separation from the slightly increased $1S(e)$-$1S_{3/2}(h)$ bleaching band becomes manifest. The bleaching spectrum (empty squares) at 0.3 ps time delay is well described by two Voigt functions at 2.01 and 2.05 eV (dotted lines) as shown in the inset of Fig. 1(c).

The recovery of the bleaching is shown at 200 fs delay intervals in Figs. 2(a)–2(c). Although the $1S(e)$-$2S_{3/2}(h)$ bleaching band is not seen so clearly as in the build-up regime, its contribution is evident from the bandwidth increase to the high-energy side with decreasing excitation photon energy. The slight redshift of the $1S(e)$-$1S_{3/2}(h)$ bleaching band has been also observed in the femtosecond nonlinear transmission spectra of CdS nanocrystals.[14] This behavior has been explained by the increasing contribution from the transition coupling a shallow hole trap to the lowest electron quantized state.

Another feature observed in the transient absorption spectra is the increase of the photoinduced absorption extending from the band-gap energy to less than 1.8 eV. The photoinduced absorption band has been generally attributed to the surface states.[16] In particular, it has been recently suggested that the photoinduced absorption originates from the transition of the electrons trapped in the lower surface states to the higher unoccupied surface states,[17] based on the quasi-continuous surface states in energy distribution due to the strong electron-phonon coupling in nanocrystals.[18]

Compared with the $1S(e)$-$1S_{3/2}(h)$ bleaching band in case of 2.20 eV photoexcitation, the enhanced bleaching band after excitation at 2.04 eV indicates a relatively large accumulation of the photoexcited carriers in the state. Since the number of hot carriers is kept constant at each excitation photon energy, the trapping of carriers should be considered, especially in the case of excitation at high-photon energies. The surface states cannot be responsible for this carrier trapping. If the electron trapping into the surface states would decrease the $1S(e)$-$1S_{3/2}(h)$ bleaching band after photoexcitation at high-photon energy, the photoinduced absorption, which originates from the electron transitions in the surface states, would increase with the photoexcitation energy. How-

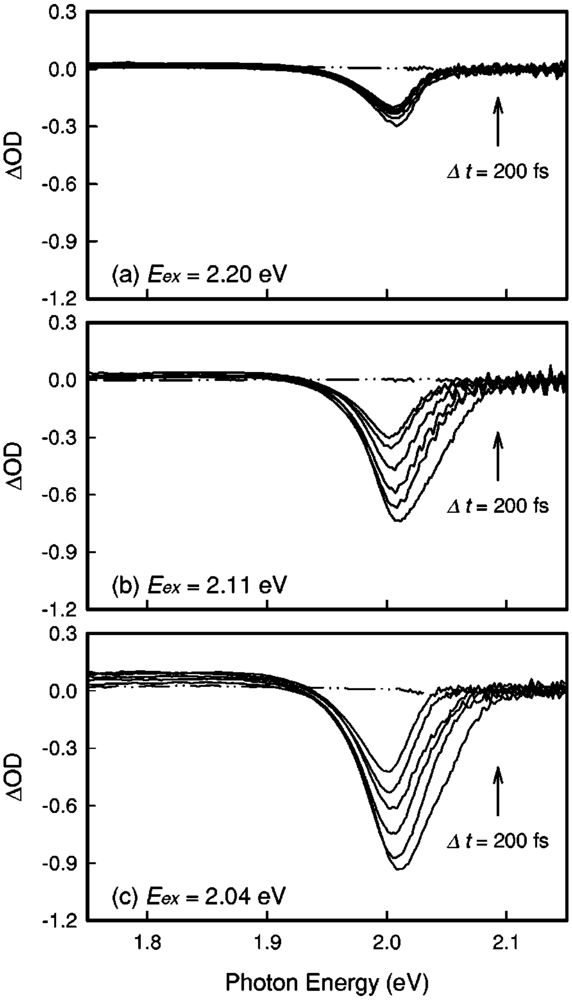

FIG. 2. The bleaching recovery of the $1S(e)$-$1S_{3/2}(h)$ and $1S(e)$-$2S_{3/2}(h)$ states and the build up of the photoinduced absorption below the band gap in the $CdS_{0.4}Se_{0.6}$ nanocrystals excited at (a) 2.20 (565), (b) 2.11 (590), and (c) 2.04 eV (610 nm).

ever, the photoinduced absorption is observed to decrease consistently with increasing excitation photon energy (Fig. 2).

Another possible trapping channel can be glass electronic states in the host glass matrix. The glass electronic states have been suggested to explain mainly photodarkening effect in semiconductor-doped glasses.[12] According to the previous report, the electrons highly excited from both confined and surface states can be trapped into the glass electronic states in the vicinity of the nanocrystals. The trapped electrons impede the population of the states through the repulsive Coulomb interaction. Consequently, the luminescence from the photodarkened CdS_xSe_{1-x} nanocrystals excited at the lowest excited electronic state has been observed to be suppressed.

In our experiment, the bleaching reduction due to the photodarkening effect has been also observed. In particular, we have tried to measure the nonlinear transmission with increasing intensity at photoexcitation energies of 2.20 eV (565 nm) and 3.10 eV (400 nm). However, severe photodarkening effect has obscured the observation of the $1S(e)$-$2S_{3/2}(h)$ bleaching. Therefore, to avoid sample degradation during the experiment, the bleaching spectra in Figs. 1 and 2 were measured after carefully checking the absence

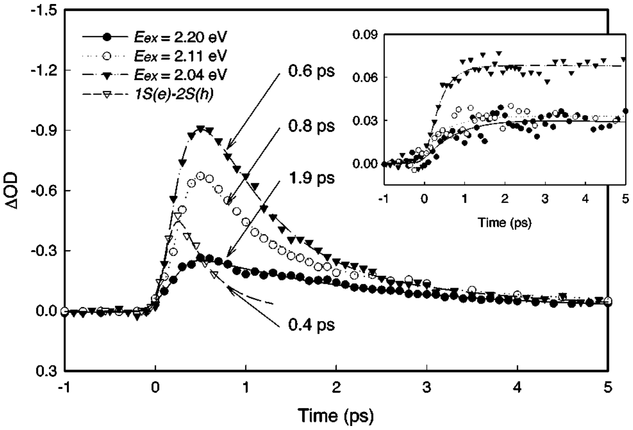

FIG. 3. The bleaching dynamics of the $1S(e)$-$1S_{3/2}(h)$ state. The ultrafast dynamics of the $1S(e)$-$2S_{3/2}(h)$ bleaching state is shown for 2.04 eV excitation. The inset shows the temporal profiles of the photoinduced absorption.

of any noticeable changes due to the darkening effect. Since the saturation of the Coulomb screening is mainly caused by the electrons trapped in the vicinity of the nanocrystal surfaces, however, further trapping into the glass electronic states is expected, especially for the electrons having enough kinetic energy to permeate farther into the glass matrix. Therefore, we conclude that, as the photoexcitation energy increases, the electron trapping into the glass electronic states has significant effect on the bleaching spectra by reducing the number of electrons relaxed into the $1S(e)$-$1S_{3/2}(h)$ state.

This statement is also supported by the fact that the $1S(e)$-$2S_{3/2}(h)$ bleaching state at 2.05 eV shows consistent behaviors. For the excitation at 2.20 eV, the bleaching band is not observed. As the photoexcitation energy decreases, however, the contribution of the $1S(e)$-$2S_{3/2}(h)$ bleaching band increases so that the band is separated from the $1S(e)$-$1S_{3/2}(h)$ state (Fig. 1) and the bandwidth is increased to the high-energy side (Fig. 2). The absence of the $1S(e)$-$2S_{3/2}(h)$ bleaching in the nanocrystals excited with low intensity [inset of Fig. 1(b)] enables us to exclude the possibility of resonance effect. Therefore, the $1S(e)$-$2S_{3/2}(h)$ bleaching is found to be also significantly affected by the electron trapping into the glass states.

Figure 3 shows the temporal profiles of the $1S(e)$-$1S_{3/2}(h)$ and the $1S(e)$-$2S_{3/2}(h)$ bleaching states, together with the build-up dynamics of the photoinduced absorption in the inset. The build-up of the photoinduced absorption with increasing excitation photon energy becomes slightly slower due to the energy relaxation within the quasicontinuous surface states. The induced absorption decreases since the increased trapping rate into the glass states makes less electrons available in the surface states. The dynamics of the $1S(e)$-$2S_{3/2}(h)$ bleaching can be extracted from the fitting results using two Voigt functions in case of 2.04 eV excitation [see the inset of Fig. 1(c)]. The rise and decay time constants are estimated to be ~ 0.2 ps and ~ 0.4 ps, respectively. Based on the report that the excited holes relax very quickly through dense and almost continuous valence-band spectrum,[20] the ultrafast dynamics assures the assignment of the bleaching band at 2.05 eV to the $1S(e)$-$2S_{3/2}(h)$ state.

The rise time of the $1S(e)$-$1S_{3/2}(h)$ bleaching band is estimated to be ~300 fs, almost independent of the excitation photon energy (or at least not resolved in our experiment). The fast buildup time is consistent with the previous report on the subpicosecond $1P$-to-$1S$ electron relaxation dynamics in CdSe nanocrystals.[15] In contrast with the build-up dynamics, the decay time constants of the bleaching band are strongly dependent on the excitation photon energy. With decreasing photoexcitation energy, the temporal profiles exhibit faster decay dynamics. It should be emphasized that the dynamics can be directly compared with each other since the excited carrier density was kept constant by adjusting excitation energy density to compensate the different optical density at each excitation photon energy. The enhanced bleaching recovery with decreasing photoexcitation energy provides further evidence for the increase of carrier population in the confined states. The ultrafast carrier dynamics of nanocrystals under strong laser excitation has been reported to originate from the nonradiative Auger process.[14] Therefore, the faster bleaching recovery with decreasing photoexcitation energy results from the increase in the carrier density due to the reduced trapping rate into the glass states.

In summary, we have investigated the effect of electron trapping into the glass electronic states on the carrier dynamics of $CdS_{0.4}Se_{0.6}$ nanocrystals excited at various photon energies by using femtosecond pump-probe spectroscopy. We have observed that, as the photoexcitation energy decreases, the bleaching of $1S(e)$-$1S_{3/2}(h)$ and $1S(e)$-$2S_{3/2}(h)$ transitions and the photoinduced absorption below the band gap become unusually enhanced with faster bleaching recovery of the $1S(e)$-$1S_{3/2}(h)$ state. These results indicate that the trapping of carriers becomes significant with increasing photoexcitation energy. The decrease in both photoinduced absorption and bleaching magnitudes with increasing excitation photon energy could not be easily explained in terms of the trapping into the surface states because an increase in the photoinduced absorption is expected in case of more trapping into the surface states. Therefore, we suggest that the electron trapping into the glass electronic states has significant effect on the carrier dynamics by reducing the carrier densities in both confined and surface states as the photoexcitation energy increases.

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