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Transfer times of electrons and holes across the interface in CdS/HgS/CdS quantum dot quantum well nanoparticles

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Abstract

The electron and hole trapping times in the HgS well of a 6 nm CdS/HgS/CdS quantum dot quantum well nanoparticle were determined from the rise time of the ultrafast transient absorption in the visible and IR regions as well as the trap fluorescence when the CdS core is excited. From the 1.5 ps observed rise time of the *well* fluorescence (which is determined by the trapping time of the slowest carrier) and the intraband hole IR absorption (150 fs), the electron localization time is found to be 1.5 ps while that of the hole is ~ 150 fs. This large difference in the observed dynamics of the electron and hole in crossing the CdS/HgS interface is discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The electron–hole dynamics in two-dimensional systems, in which the carrier motion is confined in one-dimension, such as semiconductor quantum wells have been extensively studied [1–4]. Studies on the size-dependent optical properties [5,6] and the electron and hole dynamics [7–9] in semiconductor quantum dots, in which the carrier motion is confined in three dimensions, have become very

active recently. At present, the CdS/HgS/CdS quantum dot quantum well (QDQW) onion-type system has been synthesized [10,11] and studied both experimentally [10–18] as well as theoretically [19–21]. The core excitation of this system leads to the relaxation of the electron and hole by crossing the CdS/HgS interface and subsequent trapping in the HgS well. Their radiative recombination leads to the observed fluorescence, which has the signature of the HgS phonon vibration [13]. The purpose of this Letter is to give the results of the time it takes the electron and hole to cross the interface and get trapped in the HgS well of this zero-dimensional QDQW system. Using ultrafast transient absorption spectroscopy by measuring the rise time of the emission from the well, the rise time of the separation of the core electron and hole and the rise time of the intraband hole absorption in the well, it was possible to determine that the

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electron trapping time is 1.5 ps while that for the hole is ~ 150 fs. This large difference in the transfer time of the electron and hole across the interface is qualitatively discussed.

2. Experimental

The CdS/HgS/CdS nanoparticles were prepared according to Mews et al. [11]. The synthesis route consists of four steps: growing of the CdS core, exchanging the Cd^{2+} ions of the outermost CdS layer of the core with Hg^{2+} ions to form the well layer, capping the HgS layer by a monolayer of CdS and finally increasing the CdS clad layer by two monolayers thus obtaining $\text{CdS}/\text{HgS}/\{\text{CdS}\}_3$ nanoparticles. The successful formation of the QDQW structure was verified by optical absorption and fluorescence measurements and transmission electron microscopy (TEM). The size of the final QDQW structure was 6 nm. To prevent aggregation of the QDQW nanoparticles, the sodium ions in the solution were exchanged by tetrabutyl-ammonium ions in a twofold dialysis process [14]. 30 ml of the colloid was then concentrated to 1 ml by vacuum evaporation at 45 °C. A few drops of that highly concentrated colloid were brought on a CaF_2 substrate and dried in a vacuum chamber for 24 h. That procedure results in a highly viscous film of nanoparticles. The absorption spectrum in the range between 400 nm and 2.5 μm revealed the absence of water, which is necessary to perform transient absorption measurement in the IR range. The absorption spectrum of the film was measured before and after irradiation. No evidence for decomposition could be found and the film sample is still stable after several months.

The laser system consisting of a regenerative amplified Ti:Sapphire laser (Clark MXR CPA 1000) is described in detail elsewhere [18]. In addition to probing in the visible spectral range the setup was modified to allow probing the spectral region between 3 and 10 μm by difference frequency generation from the signal and idler waves from an OPA (TOPAS). The IR probe pulses were detected by a nitrogen cooled HgCdTe detector (EG&G) coupled to a lock-in-amplifier (Stanford Research). Different excitation wavelengths were

generated by SHG (400 nm) and THG (266 nm) of the fundamental laser wavelength and by SHG (650 nm) and SFG (580 nm) of the signal and idler waves from a second OPA with the fundamental.

3. Results and discussion

In Fig. 1(top), the room temperature steady-state absorption and emission spectra of the $\text{CdS}/\text{HgS}/\{\text{CdS}\}_3$ nanoparticles in colloidal solution are shown. The absorption edge extends to about 720 nm, which is redshifted from the excitonic feature observed at 465 nm for the initially prepared CdS nanoparticles. Furthermore, the derivative spectrum allows us to determine the energy positions of the two strongest optical transitions in the HgS well below the band gap of the CdS core (at 465 nm). These transitions are found to have two maxima at about 640 and 525 nm.

The emission spectrum at room temperature of the $\text{CdS}/\text{HgS}/\{\text{CdS}\}_3$ QDQW colloidal solution is broad and unstructured and extends from 650 nm to lower energies. The spectrum shown in Fig. 1 was measured after growing a layer of $\text{Cd}(\text{OH})_2$ on the surface of the CdS clad, which was achieved by adding Cd^{2+} ions to the colloidal solution and increasing the pH value to 10.0 with 0.1 M NaOH solution. This leads to an increase in the fluorescence quantum yield as well as a more pronounced excitonic band gap emission in agreement with previous results [11,12]. The excitonic emission has its maximum at 730 nm, which is also in agreement with that reported by other groups [11,14]. The excitation spectrum of the emission at 760 nm is similar to the absorption spectrum of the QDQW, which shows that the absorbing and emitting species in the colloidal solution are identical. Equally important, it suggests the absence of different types of high energy nonradiative relaxation processes for the excited electrons and holes.

Fig. 1(bottom) shows the femtosecond time-resolved transient absorption spectrum of the $\text{CdS}/\text{HgS}/\{\text{CdS}\}_3$ film on a CaF_2 substrate at different delay times between the pump and the probe pulses at room temperature. The sample was excited at 400 nm, where the film has an absorbance of 1 OD. The transient absorption spectrum taken

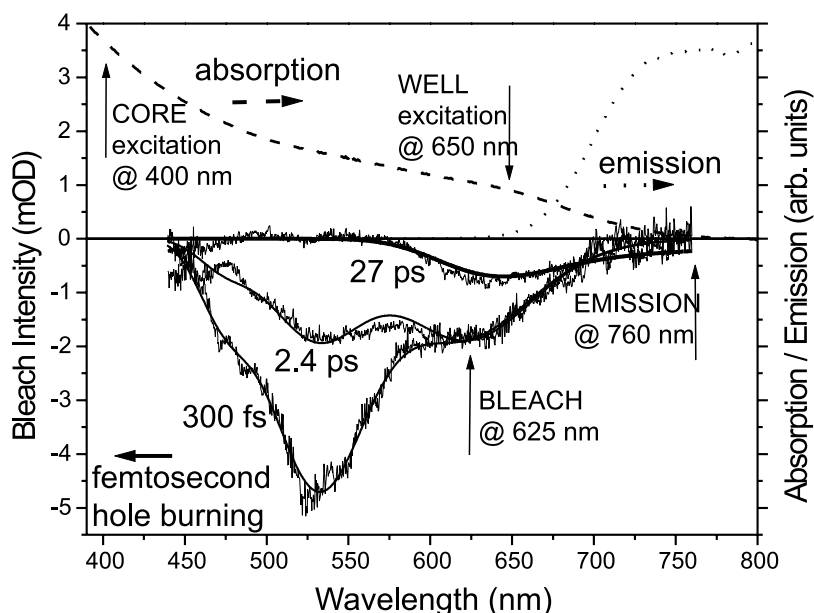


Fig. 1. Top: steady-state absorption (—) and emission (···) spectra of the colloidal solution of CdS/HgS/{CdS}₃ QDQW nanoparticles at room temperature. Bottom: time-dependent bleach (negative absorption) spectra of a film of CdS/HgS/{CdS}₃ nanoparticles on a CaF₂ substrate at room temperature at different delay times between the pump (400 nm) and probe pulses. (The absence of the negative bleach below 450 nm is due to the fact that the monitoring continuum does not have intensity there.)

immediately after the pump pulse shows several negative absorption (i.e., bleach) bands over the whole visible range and a very weak stimulated emission signal. The positions of these bands were determined by a simultaneous fit of the three spectra to 5 Gaussian curves with maxima at 470, 530, 625, 640, and 720 nm. By comparing the energy positions of the negative transient absorption (bleach) peaks to the steady-state absorption and emission (maximum at 730 nm) the four high energy bands are assigned to a bleach signal while the weak band at 720 nm is assigned to stimulated emission. This assignment is in very good agreement with the observed maxima of the second derivative of the steady-state absorption spectrum, from which the position of the two optically allowed transitions at about 640 nm and 525 nm could be resolved. The positions of the bleach bands are also in good agreement with the calculations by Jaskolski and Bryant [20] and allow an assignment of the transitions to $1S-1S_{3/2}$ (720 nm), $1P-1P_{3/2}$ (640 nm), $1P-1P_{1/2}$ (625 nm), and $1S-2S_{3/2}$ (530 nm). Our observed higher energy al-

lowed transitions have not yet been calculated. It should further be mentioned that the assignment of the last bleach feature to a stimulated emission is further supported by the fact that a negative transient absorption could be recorded at even longer wavelength (>760 nm) than shown in the transient absorption in Fig. 1 where the ground state absorption is already zero.

The femtosecond time-resolved transient absorption spectra of the QDQW particles in Fig. 1 further show the spectral diffusion of the optical hole in the CdS/HgS/{CdS}₃ nanoparticle film as the signal decays faster at shorter wavelengths. This is in agreement with several previous femtosecond studies [16–18] performed on colloidal solutions of CdS/HgS/CdS nanoparticles with a different thickness and different number of the HgS well. The decay times of the bleach bands at the lowest optical transitions at energies 720 nm ($1S-1S_{3/2}$) and at 640 nm ($1P-1P_{3/2}$) involving the $1P$ and $1S$ electrons in the range of tens of picoseconds can be explained by trapping the electron and hole in shallow and deep traps. The radiative

recombination of electron and hole is much slower and extends from the nanosecond to the microsecond range as observed in time-resolved fluorescence measurements [12].

The rise times of the transient absorption signals at different wavelength as a function of the excitation wavelength are determined. Fig. 2 shows the rise times of the transient absorption signals at 625 nm (bleach), 760 nm (stimulated emission), and 4.7 μm (induced absorption) of the QDQW nanoparticle $\text{CdS}/\text{HgS}/\{\text{CdS}\}_3$ after excitation with 400 nm into the CdS core. The rise times of the ground-state bleach at higher energies were also measured at 470, 525, and 560 nm. All four bleach signals have rise times between 200 and 300 fs, which is summarized in Table 1. On the other hand, the stimulated emission signal rises in 1.5 ps, which is much longer than the bleach rise time. The rise time of the positive IR transient absorption signal at 4.7 μm is shown in Fig. 2. This is found to be 150 fs, which is similar to the ground state bleach bands. This absorption is well below the HgS band gap absorption and thus must be assigned to an intraband transition.

Upon optical excitation directly in the HgS well states at 650 nm, the rise of the bleach, the stimulated emission signals as well as the intraband IR absorption at 4.7 μm could not be resolved from the pulse width of the pump and probe pulses (100 fs) as shown in Fig. 3. From the resolution of the optical delay line (21 fs) and the laser pulse width (100 fs), an upper limit of the rise times of these signals are found to be <50 fs. It should be mentioned that excitation at 580 nm, which also excites states within the HgS well, leads to a similar fast rise of all the transient signals recorded. However, excitation at 266 nm into even higher energetic core states leads to similar results as those observed from the 400 nm excitation (see Fig. 2). It is therefore concluded that the difference between the rise times observed when excitation is carried out at different energies must result from different dynamics of the charge carriers. Excitation at higher energies separates electron and holes in the core followed by relaxation that involves crossing the CdS/HgS interface, which increases the transport time.

The above observations show that the rise times of the four bleach signals and the stimulated

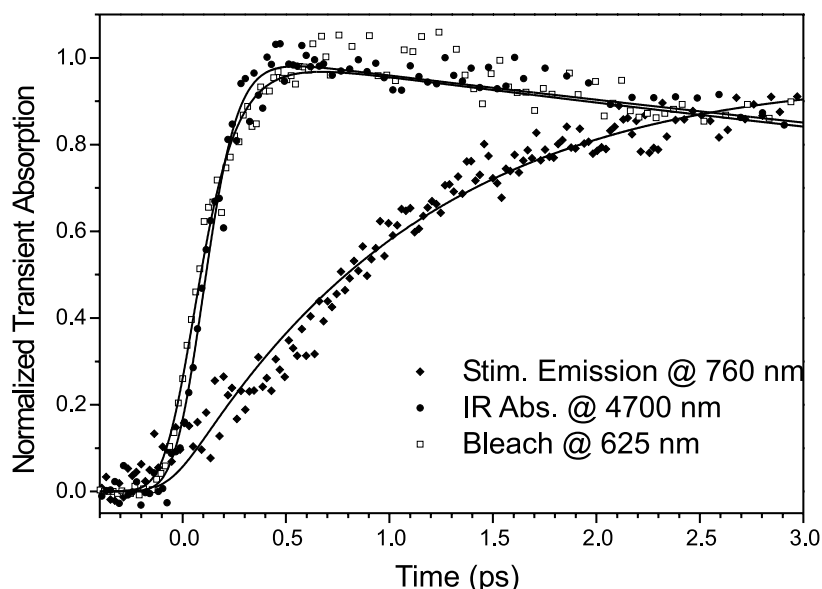


Fig. 2. The rise of the negative transient absorption (bleach) signal at 625 nm (\square : $\tau_{\text{rise}} = 280$ fs), of the stimulated emission at 760 nm (\blacklozenge : $\tau_{\text{rise}} = 1.5$ ps), and of the intraband induced absorption at 4.7 μm (\bullet : $\tau_{\text{rise}} = 150$ fs) of the $\text{CdS}/\text{HgS}/\{\text{CdS}\}_3$ QDQW nanoparticles after excitation at 400 nm (into the CdS core absorption). From these results the electron and hole trapping times are determined.

Table 1

Summary of the rise times of the bleach, stimulated emission and induced IR absorption after excitation into the core and well of the QDQW nanoparticles

Excitation	470 nm	525 nm	560 nm	625 nm	760 nm	4700 nm
Core: 400 nm	200 fs	240 fs	215 fs	280 fs	1500 fs	150 fs
Well: 650 nm	<50 fs	<50 fs	<50 fs	<50 fs	<50 fs	<50 fs

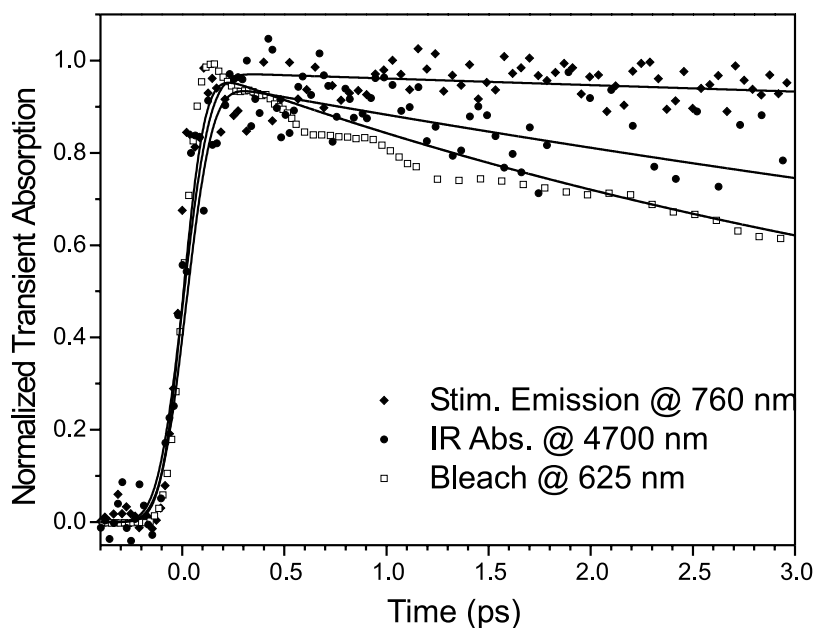


Fig. 3. The rise of the negative transient absorption (bleach) signal at 625 nm (\square : $\tau_{\text{rise}} = 50$ fs), of the stimulated emission at 760 nm (\blacklozenge : $\tau_{\text{rise}} = 50$ fs), and of the intraband induced absorption at 4.7 μm (\bullet : $\tau_{\text{rise}} = 50$ fs) of the CdS/HgS/ $\{\text{CdS}\}_3$ QDQW nanoparticles after excitation at 650 nm into the HgS well absorption. The rise of the signals is limited by the width of the pump pulse (100 fs) and therefore only an upper limit of 50 fs for the rise time can be given. The longer rise times observed in Fig. 2 (when excitation is carried out in the core absorption) must then be a result of crossing the CdS/HgS interface by the charge carriers.

emission signal are not only faster than the pulse width of the laser used (<50 fs) after direct excitation in HgS well states at 650 nm, but more importantly are faster than the rise times of the same transitions after optical excitation into higher energy CdS core states (200–300 fs for the bleach and 1.5 ps for the stimulated emission). It can thus be concluded that the slower rise times observed upon 400 nm excitation correspond to the localization (trapping) of the excited charge carriers (electron and hole) from the CdS core into the HgS well. Based on the steady-state absorption and emission spectra in Fig. 1 the observation

wavelengths of 625 and 760 nm correspond to HgS well states as already discussed above. Therefore, the rise times of these signals indicate the occupation of levels in the HgS well.

The induced IR absorption signal at 4.7 μm shows a similar bi-exponential decay behavior as the bleach signal at 625 nm. The rise time of the signal after direct excitation of HgS well states at 650 nm is <50 fs, similar to the visible bleach signals. Furthermore, a rise time of about 150 fs is observed when excitation is carried out at 400 nm comparable to the bleach rise times. Therefore the induced absorption signal at 4.7 μm has the same

rise and decay behavior as the bleach signal of the HgS well transitions³. This indicates that the same charge carrier is responsible for both signals.

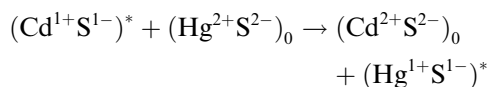
According to the state filling model [7], the *bleach* in semiconductor nanoparticles is due to the occupation of previously empty levels by an excited electron or the presence of a hole for an electronic level, which was occupied before optical excitation. Bleach therefore occurs when one of the charge carriers is transferred to the levels between which the band gap transition takes place in the HgS well. The bleach rise times of 200–300 fs must then correspond to the localization time of the charge carrier which can cross into the well more easily and hence faster.

It is established that the emission in this system takes place as a result of radiative recombination of the electron and hole in the HgS well [17,18]. Thus for the *emission* process to take place, both charge carriers need to be present in the HgS well in order to recombine radiatively. Thus the rise time of the stimulated emission signal of 1.5 ps after excitation of the CdS core states at 400 nm is determined by the localization time of the charge carrier with the slower localization probability in the well.

Based on theoretical calculations for the QDQW system [20] the *IR absorption* signal can be assigned to the hole intraband transition. The results of these calculations give an energy difference of about 0.28 eV between the lowest hole state $1P_{3/2}$ and the $1S_{3/2}$ state, which corresponds to a transition wavelength of 4.4 μm . This fits reasonably well with the observed absorption at 4.7 μm . According to the theoretical calculations the energy difference between the two lowest electron states in the conduction band is 0.37 eV (transition wavelength of 3.3 μm). Thus the IR probe pulse at the chosen wavelength is not expected to interact with the electrons in the conduction band. The rise time of the observed IR absorption at 4.7 μm of 150 fs can therefore now be assigned to the local-

ization time of the hole in the HgS well. This thus leads to the conclusion that the electron localization time in the well is 1.5 ps.

This large difference in the transfer time of the electron and hole across the CdS/HgS interface can be explained in the solid state language as follows. The effective mass of the hole in the valence bands of CdS and HgS are quite similar [20], in contrast to the effective mass of the electron in the conduction bands in the two materials. This makes it easier for the hole to cross the interface than the electron. Of course, the use of effective mass language might not be quite appropriate in this nanostructure in which the well does not even have a full unit cell. Since nanoparticles are in between solids and molecules, one may use a molecular language. A possible explanation for the much faster transfer rate of the hole compared to the electron across the interface can then be given as follows. The ground state of the CdS and HgS can be thought of having the $M^{2+}S^{2-}$ ionic structure. The excited state could be approximated by $M^{1+}S^{1-}$, i.e., the excitation is considered as an electron transfer from S^{2-} to M^{2+} and a hole transfer from M^{2+} to S^{2-} . Thus, the transfer of the charge carriers from the $(Cd^{1+}S^{1-})^*$ excited state to the ground state of the HgS $(Hg^{2+}S^{2-})_0$ involves the hole transfer from S^{1-} of the $(Cd^{1+}S^{1-})^*$ to the S^{2-} of the $(Hg^{2+}S^{2-})_0$ and an electron transfer from Cd^{1+} of CdS to the Hg^{2+} of HgS according to



It is obvious that the hole transfer process is a charge resonance process between sulfur ions and is expected to be more rapid than the electron transfer process which is between *different types of ions* and would therefore need to be assisted by phonon processes which reduce the transfer rate. In the electron transfer language, the Franck–Condon factors are expected to be much larger for the hole transfer than the electron transfer which leads to a faster transfer rate for the hole. Furthermore, the density of hole states in the valence band is much higher due to the degeneracy of the p-orbitals of the sulfur ions. Since the rate of the observed charge transfer processes are related to

³ The faster rise of the IR absorption (150 fs) compared to the bleach (250 fs) can be explained if it is assumed that the initially excited core electron and hole states also give rise to an IR absorption due to intraband transitions.

the Franck–Condon factors as well as the density of states, one would expect a faster hole transfer in agreement with our experimental results.

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