Recombination processes in CdTe quantum-dot-doped glasses

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Electron-hole recombination in CdTe quantum dots was studied by photoluminescence and resonant femtosecond pump–probe measurements. A dependence of recombination times with pump pulse intensity was observed and we attribute this to the Auger recombination process. The overall kinetic processes that we observed are a fast decay from the initial excited state to surface trap states, the Auger recombination, the recombination of electrons from the surface states, and a longer time recombination which we attribute to electrons in the deep traps states. © 2004 American Institute of Physics. [DOI: 10.1063/1.1801683]

Semiconductor quantum dots (QDs) have attracted attention because they exhibit large optical nonlinearities as well as fast response times (less than 1 ps) potentially useful for optical devices.1–4 Applications of quantum dots in laser emitters, optical communications, switching elements, and nanocrystalline solar cells5 have been reported. Different methods of preparation have been developed to synthesize the QDs in both colloidal and solid-state forms, with narrow-size distributions.6 Special attention has been devoted to QDs formed from II–VI semiconductors such as CdTe, CdS, CdSe, and CdS,Se1–x.

The nonlinear and luminescent properties of QDs are affected by carrier dynamics. Carrier trapping and nonradiative Auger process are believed to play a major role in the early stages of ultrafast dynamics of the relaxation of those carriers. The QD photoluminescence spectra usually present two broad bands: one at the band edge, due to the direct recombination, and the other at lower energies, that has been attributed to electron-hole recombination involving deep defect or surface trap states.7–9

In this letter, we reported pump–probe measurements of recombination processes in CdTe QDs doped borosilicate glass as a function of the pump pulse intensity. We observed at least three recombination processes depending on the pump intensity. A rate equation model considering the Auger recombination process describes well our relaxation data as a function of pump intensity. Bulk CdTe is a direct band gap semiconductor with band gap of 1.5 eV and a Bohr exciton radius of 7.5 nm, large when compared to CdS and CdSe. Therefore, CdTe QDs are expected to show a stronger quantum confinement and enhanced nonlinear optical properties. Our QDs photoluminescence spectra show the presence of surface traps through a broadband in the near infrared and no peak at higher energies, suggesting that recombination from deep traps, or defect states, are more important than direct recombination for CdTe quantum dots.

CdTe QD doped glass was produced by melting the glass components, SiO2, Na2O, B2O3, ZnO, Al2O3, together with metallic Te and CdO dopants.5,10 The QDs are produced in a subsequent heat treatment of 640 °C for 77 h. Due to this long heat treatment, the average radius of the QDs was 7.2 nm. We used a pump–probe setup to study the ultrafast response of the sample. The pulses were generated from a tunable femtosecond Ti:sapphire laser operating at 80 MHz pumped by an argon laser. The pump and probe pulses were split from the Ti:sapphire laser output in the ratio \( I_pump/I_{probe} = 20:1 \), polarized perpendicularly to each other to avoid coherent artifacts, and chopped at different frequencies, \( f_pump \) and \( f_{probe} \). The lock-in was synchronized at \( f_pump + f_{probe} \) to guarantee that the signal detected was generated only by a joint pump and probe effect. The two beams were focused on the same spot in the sample with a spot size of about 10 μm by a lens of focal length 5 cm. The transmitted probe passes through a polarizer to block light scattered from the pump beam and detected by a pin detector connected to the lock-in amplifier. All measurements were performed at room temperature.

The photoluminescence (PL) and absorption spectra are shown together in Fig. 1, which demonstrates the absence of PL peaks near the band edge, but only the broadband spectrum at lower energies, in the near-infrared range. This strongly suggests that the recombination in this sample happens from the deep traps states rather than from the electron-hole direct recombination from the confined levels.11 For the

\[ \text{FIG. 1. Absorption and photoluminescence spectra of CdTe quantum dots.} \]

It can be noticed that there is not peak at band edge in the photoluminescence spectrum.
FIG. 2. Transient transmission signals at different pump pulse intensities.

7.2 nm radius the confinement is not so strong and effects as Auger recombination can excite carriers to those deep traps states.

Figure 2 shows the transient transmission signals at different pump intensities. We observe that the recombination becomes faster as the intensity of the pump pulse increases. In a bulk semiconductor the phase space filling and the Coulomb interactions between the electron-hole pairs photoexcited by the pump pulse are the main mechanisms for bleaching and for the transient transmission signals. In semiconductors QDs, however, the carriers can be trapped very rapidly at the surface due to the large surface-volume ratio. From surface states the evolution of the trapped carriers involves several processes and all of them can contribute to the relaxation. The Auger recombination process is a three carrier process involving two electrons and one hole or one electron and two holes, in which the energy released by one carrier that falls to lower levels is immediately transferred to the other carrier, that rises to higher levels. The energetic electron (or hole) can dissipate its excess energy in different ways, including phonon emission, electron ejection, or diffusion to some long-lived deep trap states that have a substantial barrier. This process can be responsible, therefore, for part of the population of the deep trap states, which result in the broadband photoluminescence spectrum at the near infrared. Another possible process is the trapped electron-hole recombination. This process presents relaxation time of some picoseconds.

Considering the following processes: (i) fast carrier trapping in surface states; (ii) the Auger recombination process; (iii) trapped electron-hole recombination; (iv) and recombination from deep trap states, many authors have described the whole process of recombination with the following rate equation group:

\[
\frac{dn_i}{dt} = -\frac{n_i}{\tau_i},
\]

\[
\frac{dn_s}{dt} = -\frac{n_s}{\tau_s} - cn_i^3 + k_s n_i / \tau_i,
\]

\[
\frac{dn_d}{dt} = -\frac{n_d}{\tau_d} + k_d n_s,
\]

\(n_i, n_s, n_d\) referring to the population in the initial excited, surface and deep trap states, respectively. As no peak was observed at the band edge in the photoluminescence spectrum, the radioactive decay from the initial excited electron-hole state to the ground state is reasonably neglected. The times \(\tau_i, \tau_s, \) and \(\tau_d\) refer to the relaxation times from initial excited state to the surface states, from surface states to ground state, and from deep trap states to ground state, respectively. The constant \(c\) is the Auger constant and the second term on the right-side of Eq. (2) represents the Auger recombination. Factors \(k_s, k_d\) are introduced to express that only a fraction of free carriers in the initial state is trapped in the surface and only a fraction of the carriers trapped in the surface states diffuses to deep trap states as a result of Auger process. Figure 3 shows these processes.

Brito Cruz et al. have measured \(\tau_d\) of about 360 fs in resonant excitation for similar samples. Considering that \(\tau_i\) is about some picoseconds and \(\tau_s\) is about a microsecond or millisecond, we can use the approximations \(\tau_i \ll \tau_s \ll \tau_d\) and \(n_i(0)=n_d(0)=0\), to obtain:

\[n_i(t) = n_i e^{-t/\tau_i},\]

\[n_s(t) = \frac{k_i n_i (1 - e^{-t/\tau_i}) e^{-t/\tau_s}}{[1 + c(k_s n_i)^2 \tau_s (1 - e^{-t/\tau_i})^2 (1 - e^{-2t/\tau_s})]^{1/2}}.\]

Because we are only interested in processes that occur at times faster than nanoseconds, we can consider \(n_d\) constant. The transmittance \(T(t)\), proportional to the population in the excited states, can be expressed as:

\[T(t) = a_i \frac{n_i}{n_0} + a_s \frac{n_s}{n_0} + a_d \frac{n_d}{n_0}.\]

where \(a_i, a_s, a_d\) are constants that indicate how important the populations are for the transmission. As \(n_d\) is approximately constant the last term in Eq. (6) is a constant, \(\beta\), which refers to the baseline in the transient transmission signals. To understand the evolution of the carriers, we can study Eq. (6) in two different moments:

(i) For \(\tau < \tau_i\), terms like \(\exp(-t/\tau_i)\) go to one, and \(T(t)\) is given by

\[T(t) = (a_i - k_i a_i) e^{-t/\tau_i} + (k_d a_d + \beta).\]
This refers to the situation of the decay from the initial excited states to the surface states.

(ii) For times much longer than \( \tau \), the terms \( \exp(-t/\tau) \) go to zero and the transmission is given by:

\[
T(t) = \frac{k_s a_s e^{-t/\tau}}{[1 + c(k_{n0})^2 \tau_s (1 - e^{-2t/\tau_s})]^{1/2} + \beta.}
\]  

Equations (7) and (8) fit well our experimental data, as shown in Fig. 2. From Eq. (7) we find a fast initial time decay \( \tau_s = 240 \) fs. This decay is followed by a third-order process, the Auger recombination, and successively by a slower decay, which refers to the trapped electron-hole recombination from the surface states. From Eq. (8) we can find both \( c(k_{n0})^2 \) \( (k_{n0} \) refers to the maximum population in the surface states) and \( \tau_s \). The adjustment shows that \( \tau_s \), which represents the recovery of electrons or holes from surface states to the ground state, is independent of laser intensity and it is about 2.1 ps. On the other hand, \( c(k_{n0})^2 \) must vary as the pump power because \( k_{n0} \) is proportional to the pump intensity in the range. Figure 4 shows how \( c(k_{n0})^2 \) varies with the pump intensity, and that the more intense is the pump pulse, the more influent is the Auger recombination.

From the data in Fig. 4 we found a slope of 2.1 ± 0.3, i.e., the instantaneous decay is proportional to the square of pump intensity. This agrees with our hypothesis that the Auger recombination is responsible for the intensity dependent decay. Similar result have been found by Ai et al. in CdSe nanoclusters films.\(^{12}\) Wu et al. have shown, that the unusual excitation intensity dependence of fluorescence can be explained by the Auger process in CdTe nanoparticles.\(^{14}\)

We can estimate the initial carrier density at excited states to be \( 10^{20} \) cm\(^{-3} \) considering that each photoexcited electron-hole pair is generated by one absorbed photon, that the sample filling factor is about \( 10^{-3} \) and that the pump pulse intensity is 3.2 GW/cm\(^2\). Using this density and the values of \( c(k_{n0})^2 \) obtained through Fig. 4, we find that the Auger constant \( c \) is about \( 10^{-29} \) cm\(^6\) s\(^{-1}\). This value is consistent with the reported ones for other II–VI semiconductors quantum dots such as CdSe and CdS.\(^{12}\)

The last term that needs to be analyzed is the baseline \( \beta \) in Eq. (8). This term corresponds to the long-lived electrons in the deep trap states. Due to the high repetition rate of the pump pulses, 80 MHz, that population is unable to fully recover and the carriers accumulate in those states. From surface states, carriers can recombine to the ground state, with time constant of 2.1 ps, or can be excited or dissipate to deep trap states and remain there for more than microseconds, resulting in the baseline in the transient transmission signals. These carriers lose a fraction of their energies in a nonradiative process, like phonon interactions, and then recombine, giving rise to the broad band in the photoluminescence spectrum at near infrared.

Finally, it is important to note that, although in CdTe QDs the recombination processes are similar to those showed by Ai et al.\(^{12}\) for CdSe nanocluster films, we found that all processes are faster in CdTe than in CdSe. Besides, by the transient transmission signals, we are able to notice that in CdTe the term with the population in the initial excited states is the most important term for the transmission, which was not true for CdSe.

In conclusion, we have studied the femtosecond dynamics of the photoexcited charge carriers of CdTe QDs doped glass and found that the carrier dynamics in CdTe QDs depend on the pump intensities. We can describe well our experimental data by considering four recombination processes: electron-hole fast decay (240 fs) from initial excited state to surface states, Auger recombination, surface trapped electron-hole recombination to ground state and recombination from deep trap states to ground states. The Auger and recombination from surface states processes allowed us to understand the processes that cause both the dynamics dependent to the pump intensity, the deep trap states population and, consequently, the broad band in the photoluminescence spectrum at near infrared.

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