Intraband Ultrafast Relaxation in CdTe Quantum Dots Dispersed in a Glass Matrix

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We present a study of the relaxation process between the discrete carrier levels of CdTe quantum dots, and its influence on the optical absorption spectrum. The evolution of the state populations is modeled by means of the rate equations for the system. Including homogeneous and inhomogeneous broadenings, we calculate the dynamic spectral hole-burning when some quantum dots are excited to states other than those involved in the lowest lying discrete transition. We compare it with experimental data of time-resolved differential transmission spectroscopy in a femtosecond scale, obtained through the pump and probe method. The samples were CdTe quantum dots doped glasses. Alterations of the absorption in all the probe spectrum ($\sim$ 200 meV) are seen. During the first moments after the excitation reaches the sample, a shift to the infrared in the bleaching is also observed. We believe this is due to a relaxation process described here.

I. Introduction

This work is intended to interpret results of Time-Resolved Differential Transmission Spectroscopy (DTS) on samples of CdTe quantum dots (QDs) doped glasses. Alterations of the absorption are observed in a wide spectral range. Two features characterize the evolution: 1) a complete recuperation of the DTS signal on times lesser than 500 fs (probably, due to trapping of carriers in surface states); 2) an infrared-shift of the bleaching, with time constant of tens of femtoseconds. We believe this last feature is generated by intraband ultrafast relaxation of the carriers. We study the evolution of the spectral hole- burning caused by this process, and compare it with the experimental results.

II. Experimental results

The experimental data (see Fig. 1) was obtained using a pump and probe configuration. The pump pulse was 60 fs long and centered at 625 nm (7 nm of spectral width). The probe pulse, weaker than pump (just for monitoring changes in the sample), was 12 fs long and with "white" spectrum. The positive sign for DTS corresponds to an increase of transmission. For large negative delay times (probe before pump), the absorption spectrum shows no alteration. For negative times, on the order of pump width (e.g. - 40 fs), we begin to have an increased transmission in the whole range of the probe spectrum. For 0 fs we have a spectral hole, that shifts to lower energies when increasing the delay time. This shift is what we are trying to explain.

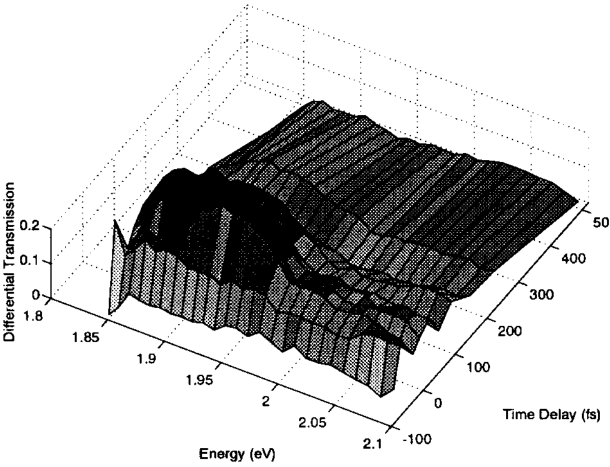

Figure 1. 3D-plot of experimental DTS showing the time dependence of spectra bleaching. Each spectra is for -60, -40, 0, +20, +50, +80, +120, +190, +255 and +520 fs delay times of the probe relative to the pump. The energy range corresponds to available probe spectrum.

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III. Linear absorption and electronic structure

Fig. 2 shows linear absorption spectrums of the samples. They consist of discrete (due to quantum confinement) optical transitions, homogeneously and inhomogeneously broadened. The last one is dominant, given the size dispersion present in these samples (10%)[2]. Fig. 2 also shows fittings that we have done to extract the oscillator strengths of the transitions. We have used previously calculated energy size dependencies of the discrete electronic states of the QDs[3] (see Fig. 3). They were verified experimentally by the PLE technique[4]. The Modified Multiband Envelope Function Theory[5] was used in this calculation, taking in consideration band mixing and non- parabolicity effects.

IV. The dynamic model

The DTS signal of Fig. 1 is produced, due to Pauli exclusion principle, by the state-filling of the energy levels, directly or indirectly induced by the pump pulse. Fig. 2 shows the pump spectrum. It overlaps three of the inhomogeneously broadened lines. This means that three different *groups* of sizes are excited. Each group is excited in resonance with one of the three lowest-lying optical transitions, that we denominate A, B, and C, respectively (see Fig. 3).

A and B transitions have the same final state: $e1^+$. This complicates the interpretation of the measured signal by the following fact: when one of these transitions is excited, the filling of the common state produces *replicas* in the DTS[6] (bleaching of the not excited transition sharing that state).

In the case of B and C excited QDs, intraband relaxation processes would depopulate the initially excited states, populating others of lesser energy (closer to the band extremes), generating more bleaching there. The overall process would cause a shift in the DTS to the low energies direction. With this idea in mind we had previously studied this effect in a phenomenological way[7]. Now we want to gain more knowledge of the physical process responsible for the relaxation. So we have studied the evolution of the electronic state populations, assigning a time constant for each relaxation (Fig. 3), and solving the rate equations for the whole system, independently for electrons and holes. We have done it for excitations of all sizes, introducing homogeneous widths for the transitions. The spectral width of the pump has also been considered. We have not considered here any other process which could drain carriers from the excited states (e. g. electron-hole recombination, transitions to traps or surface states), because our present interest is the very fast initial relaxation, only.

V. Results and discussion

In Fig. 4 we show some of our simulation results. We have used a much lesser value for τ_{h12}, than for the other relaxation times, because the electronic structure of Fig. 3 shows that the hole states involved in this transition are very close to each other. Considering the energy of LO-phonons ($\sim$ 20 meV) for “bulk” CdTe, they could be strongly coupled and this would be the mechanism responsible for the relaxation. We used an ultrashort time of 10 fs to increase the influence of it in the results. For the other transitions, the energy differences are much larger than the phonon energy. More than one phonon would be needed, decreasing the probability of the transition to occur. In spite of this, we have maintained these times on the order of hundreds of femtoseconds, to include other possible mechanisms (e. g. in [8] an Auger-like process is suggested for ultrafast intraband relaxation. We have not considered any “special” Auger term in our rate equations).

We have varied the homogeneous width to describe how the completely bleached DTS can be developed from well separated spectral holes (see the case of $\Gamma =$ 0 meV). The one near 2.1 eV is the replica of the A excited group, due to the B transition bleaching; and there is a contribution of the replica of the B excited group, due to bleaching of the A transition, in the hole near 1.88 eV. But this hole is basically generated by the relaxation processes, being dominant the population of $h1^-$ for B excited sizes. The hole near 1.8 eV is only due to the ultrafast relaxation $h1^+ h1^-$ for the C excited group.

From this figure we see that the relaxation processes we have incorporated can effectively generate an infrared-shifting of the bleaching (as we previously knew from the simpler model of [7]). But, in spite of all our cares to correctly choose the used parameters,

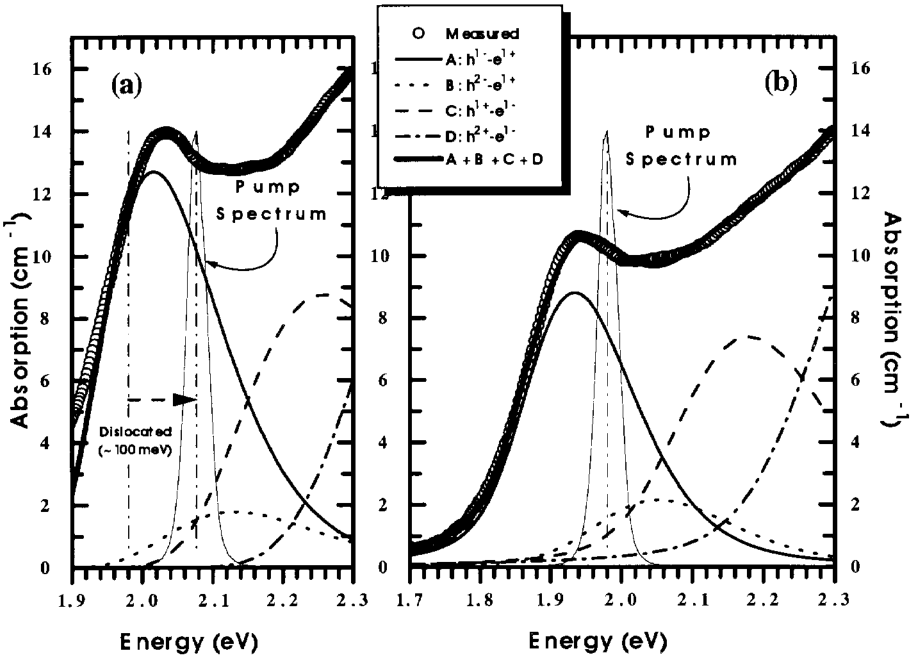

Figure 2. Measured Linear Absorption Spectrum and calculated ones for CdTe QDs doped glasses: (a) Low temperature (9 K); only inhomogeneous broadening[1] was considered. (b) Room temperature (applicable to DTS experimental conditions); all lines include *also* an homogeneous width of 60 meV (FWHM = 2Γ). In both cases (a) and (b), the oscillator strengths were chosen to minimize the quadratic error between experimental and calculated spectrums. Also shown is the pump spectrum. In (a) it is dislocated 97 meV, to consider dependence with temperature of the band gap.

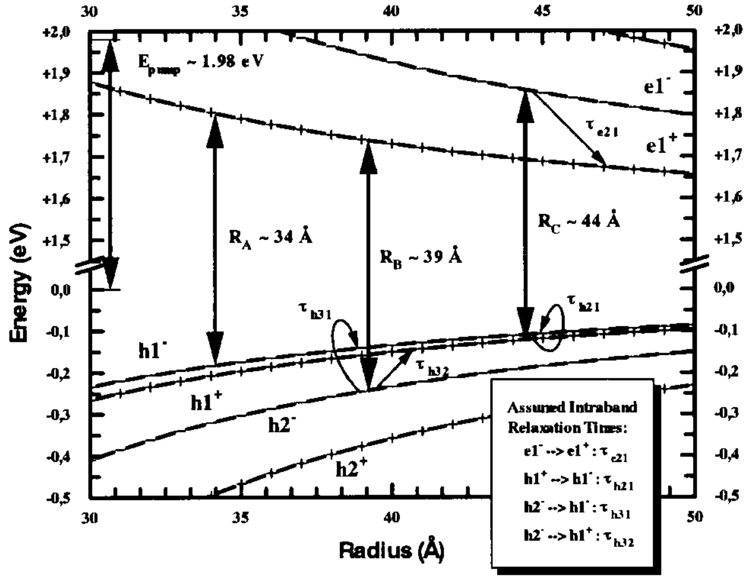

Figure 3. Size dependence of the Electronic Structure of the QDs. The break in the energy axis corresponds to the energy gap of "bulk" CdTe (~1.5 eV). For the notation of the states see[4]. The sign in this notation refers to the parity of the wave function (+ even, - odd). Only transitions involving opposite parity states are allowed. Doubled ended arrows indicate the transitions excited with the 1.98 eV pump, and for which medium sizes of QDs. Also shown are the different intraband transitions and their relaxation times.

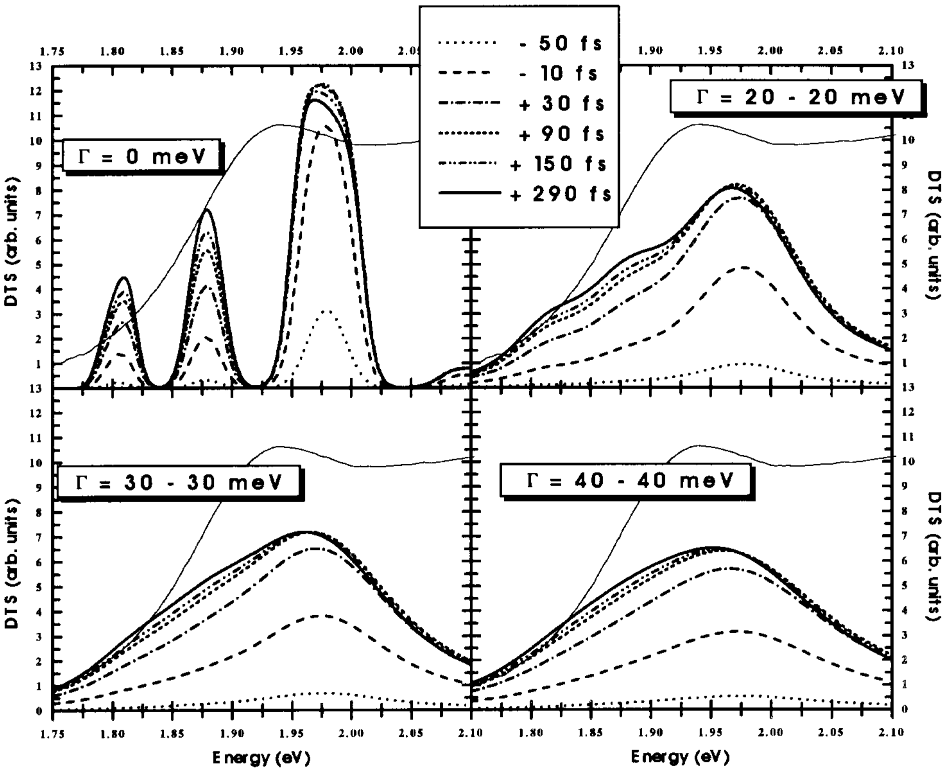

Figure 4. Simulation results for $\tau_{h21} = 10$ fs and $\tau_{e21} = \tau_{h31} = \tau_{h32} = 300$ fs. Each plot is for a given homogeneous width (FWHM = 2Γ), and shows the DTS signal for different delay times of probe relative to pump. Also shown is the linear absorption spectrum, for reference, only.

the overall relaxation signal is very weak. Fig. 5 shows that, although in the total signal we have not a great dislocation of the spectrum, considering the C-excited size group only, the dislocation could be as important as in the experimental case. The relative low quantity of QDs excited in this transition mask this signal.

VI. Conclusions

We have studied the influence of intraband relaxation processes in the DTS, modeling the dynamic of the Spectral Hole-Burning in CdTe QDs doped glasses. To do it, we have needed a definite knowledge of the electronic structure and linear absorption spectrum. We have deduced relative trusty values of Oscillator Strengths and Homogeneous Linewidth (FWHM ~ 60 meV was sufficient enough for the complete bleaching we observe in the DTS). Although great care has been taken in choosing all the simulation parameters, the dislocation of the major part of the bleaching is not so strong as in the experimental results. We recall that we based the choice of our relaxation times in the proximity of the $h1^{+}$, $h1^{-}$ states, supposing this to be sufficient for a relaxation via phonon emission. If we do not want to invoke unknown relaxation processes that let us decrease the other relaxation times of Fig. 3, we must conclude that some other effects are assisting in the observed dislocation of the DTS signal.

Until today we have been using rate equations to study the evolution of the populations, and, so, of the sample transmission. No coherent effect has been considered, what it is partially supported by the great homogeneous width obtained (low coherent times).

We have neither included relaxation processes which take carriers from the QDs states. A size dependence relaxation[9] could help the interpretation, assisting the intraband relaxation process, as we could not use it by its own. We would need size dependence of the time constants in discrepancy with the decay times of the experimental data.

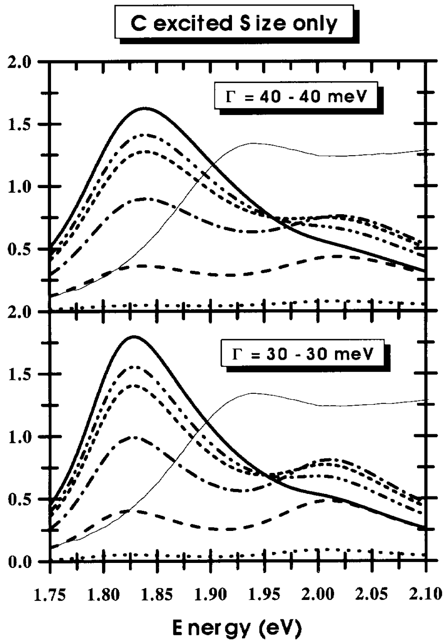

Figure 5. Same as in Fig. 4, but just the contribution of the C-excited Size Group for the indicated homogeneous width, and the same delay times as there.

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