Time-resolved Raman-spectroscopic evidence for efficient electron trapping in a photodarkened CdS$_x$Se$_{1-x}$-doped glass: Photocontrol of electrons in semiconductor microcrystallites

Xiaojie Zhang and Hiro-o Hamaguchi*

*Molecular Spectroscopy Laboratory, Kanagawa Academy of Science and Technology (KAST),
KSP East 301, 3-2-1 Sakato, Kawasaki 213, Japan*
(Received 27 June 1994; revised manuscript received 15 August 1994)

The photodynamics of a photodarkened CdS$_x$Se$_{1-x}$-doped glass has been studied by pump-probe time-resolved Raman spectroscopy. A marked decrease in the phonon Raman intensities was found when the photodarkened sample was preexcited by the pump pulse. Such changes were not found for a fresh (not photodarkened) sample. The decrease in the Raman intensities, which is related to the decrease in the number of electrons in the upper edge of the valence band, recovered with a time constant of 45 ms. This means that the electrons photoexcited by the pump pulse are trapped in a certain photodarkening-induced state and that the lifetime of this state is 45 ms. It is pointed out that we now have a means to control the population of valence electrons in semiconductor microcrystallites by adjusting the laser power and/or the delay time in pump-probe experiments.

In the past few years, CdS$_x$Se$_{1-x}$-doped glass and other analogous materials with semiconductor quantum dots have been investigated intensively and many physical phenomena have been found.[1-8] In particular, CdS$_x$Se$_{1-x}$-doped glasses have received considerable attention as a promising nonlinear material with a large optical nonlinearity[9] and a fast optical response.[10] A photoinduced irreversible process, which is often called photodarkening or laser annealing, has been found in these glasses. The photodarkening effect appears with the permanent fading of luminescence intensity and the shortening of the recombination rate of excited carriers, which is suggested to lead to a fast optical response.[11,12] The photochemical changes are permanent but can be reversed if the sample is heat treated for several hours. In addition to the studies of this effect on the carrier-recombination process,[13,14] other studies involving different experimental methods have also been performed. For example, the photodarkening effect has been related to the formation of a permanent volume grating in the optical phase conjugation experiment[12] and to the absorption nonlinearity.[15] Though several models[13-18] have been suggested to account for these observations concerned with the photodarkening effect, the relevant physics is not well understood. To obtain further information about the structure and dynamics of the photodarkened CdS$_x$Se$_{1-x}$-doped glass, we used pump-probe time-resolved Raman spectroscopy.

The experimental setup was a standard pump and probe system consisting of two Q-switched Nd:YAG (yttrium-aluminum-garnet) lasers (4–50 Hz), one for pumping (the third harmonic 355 nm, 15 ns in pulse width, 0.32–1.40-mJ pulse energy at 50-Hz repetition rate) and the other for probing (the second harmonic 532 nm, 15 ns, 0.08–0.25-mJ pulse energy at 50-Hz repetition rate). The polarization directions of the two beams were set orthogonal to each other. The time delay between the pump and the probe pulses was adjusted by an electric delay generator. The scattered light from the sample was collected by a camera lens and recorded by a gated intensified photodiode array detector after passing through a triple polychromator. The gate width was 20 ns. To avoid the sample damage, both the pump and the probe beams were only loosely focused on the sample. The spot size was 1 mm in diameter for the probe beam and 2 mm for the pump.

The experimental results presented here were obtained by using a CdS$_x$Se$_{1-x}$-doped glass with small CdS$_x$Se$_{1-x}$ microcrystallites of about 2 nm in average diameter. The S fraction determined by the Raman spectrum[1] was $x = 0.2$. The absorption edge of the lowest excitonic state, which was obtained by extrapolating the optical absorption coefficient against photon energy, was 620 nm. The sample glass, 0.25 mm in thickness, was photodarkened by irradiation of the 532-nm light for more than half an hour in advance. The photodarkening process was monitored by the intensity change of luminescence. No change was found in the stationary Raman spectrum even after the sample was photodarkened. All experiments were done at room temperature.

Figure 1 shows a typical photodarkening effect on the time-resolved Raman spectrum obtained at zero time delay between the pump and probe pulses. The intensities of the phonon Raman bands (229 cm^{-1} for the CdSe-like phonon and 298 cm^{-1} for the CdS-like phonon) decrease when the pump beam is introduced. The decrease can be seen clearly as negative dips in the difference spectrum. We also tried the same pump-probe experiment for a fresh sample by continuously moving the sample using a translation stage. In this case, no dip was found in the difference spectra.

The delay-time dependence of the Raman dip intensity of the 229-cm^{-1} band has been measured using the lowest repetition rate of 4 Hz and the pulse energy of 4 mJ. The dip intensity decreased as the delay time was increased. In a simple one-electron model, the polarizability of the microcrystallite and hence its derivatives associated with Raman intensities are proportional to the number of electrons that take part in the optical transition. In the present experiment, the observed Raman scattering with the 532-nm excitation is most dominantly contributed by the optical transition from
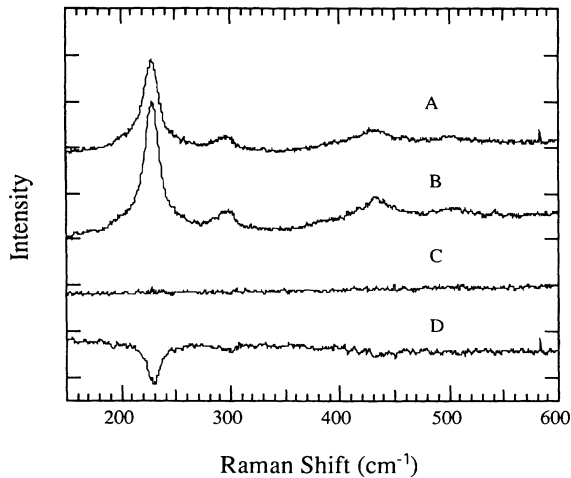
FIG. 1. The photodarkening effect on the time-resolved Raman spectrum (0-ns delay time) of a CdS_xSe_{1-x}-doped glass. A, pump and probe; B, probe only; C, pump only; D, difference $A - B$.

FIG. 3. Pump-laser power dependence of the trapping fraction κ. The probe-laser power was kept constant at 10.5 mW.

the upper edge of the valence band. Therefore the polarizability derivatives are proportional to the number N of electrons in the upper edge of the valence band and the observed Raman intensity I is proportional to N^2. Then, we can relate the Raman dip intensity ΔI with the change of the number of electrons ΔN in the valence band. The trapping fraction $\kappa = \Delta N/N$, representing the fraction of the upper-edge valence electrons that are depleted by the pump pulse, is related to the Raman intensity I and the dip intensity ΔI,

$$\kappa = 1 - (1 - \Delta I/I)^{1/2}.$$

If we plot κ vs the delay time (Fig. 2), we obtain a single exponential decay with a time constant of 45 ms. A small residual trapping fraction at 250 ms might be an indication of some extra longer-lived trap levels. The electrons excited by
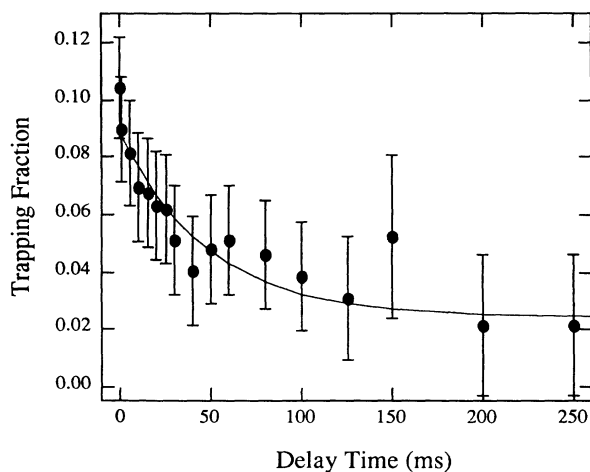
FIG. 2. Time dependence of the trapping fraction κ on the delay time. Due to the limitation in the repetition rate of the lasers, delay times longer than 250 ms were not measured.
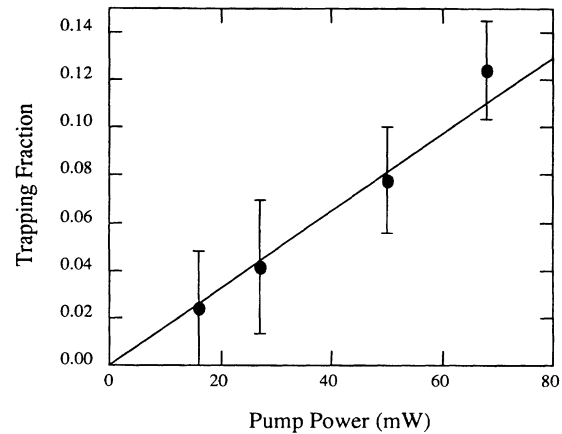
the pump pulse to the conduction band are trapped in an unknown trap state and they relax back to the valence band with the time constant of 45 ms. The fact that the Raman-intensity change was observed only for the photodarkened sample indicates that this trap level is characteristic of the photodarkening effect.

The pump-laser power dependence of the Raman dip intensity was studied in the power range of 0–70 mW. Figure 3 shows the power dependence of the trapping fraction κ determined from the dip intensity. A linear relationship is observed between κ and the laser power, indicating that the pumping of valence electrons occurs via one-photon absorption and not via any higher-order processes. It is seen from Fig. 3 that more than 10% of the upper-edge valence electrons are depleted when pump-laser power of 70 mW is used. The probe-laser power dependence of the Raman dip intensity was also examined. Although the dip intensity was proportional to the probe-laser power, the trapping fraction κ calculated from the dip intensity holds constant within experimental uncertainties. This indicates that the probe beam itself did not affect the population of electrons in the valence band.

Since there is no change in the positions and the widths of the observed Raman bands, the photodarkening effect has nothing to do with the change in the bulk lattice structure of the semiconductor microcrystallite. It is the dynamics of the photoexcited electrons that are profoundly affected by the photodarkening effect. Taking the existing model of photodarkening[13–18] into account, we explain the present time-resolved Raman observations using a simple three-level model (Fig. 4). In this model, C and V indicate the conduction band and the valence band, respectively. The third state D is a long-lived trap state formed permanently as a consequence of photodarkening. This state is most likely to be connected with the semiconductor surface state since no change in the bulk structure has been suggested from the Raman spectrum. Nonradiative decay from C to D is so efficient that the lifetime of the recombination emission is
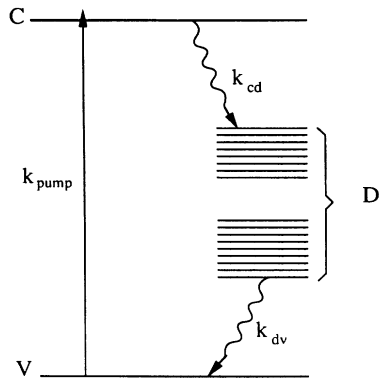
FIG. 4. A three-level model for the photodarkening effect. V, valence band; C, conduction band; D, photodarkening-induced trap state. See text for the meanings of the rate constants k_{pump}, k_{cd}, and k_{dv}.

shortened with the concomitant decrease of the intensity. If the valence electrons are photoexcited by a strong pump pulse, a significant number of electrons are promoted to C with a rate k_{pump} and then to D with a rate k_{cd}. Assuming the CdS_xSe_{1-x} volume fraction of 0.001–0.005,[19] we estimate that a few tens of electrons per microcrystallite are photoexcited by a pump pulse with 4-mJ energy and a 1-mm-diam spot. If the decay rate from D to V, k_{dv}, is small compared to k_{pump} and k_{cd}, electrons are trapped in D and the valence band is depleted. If the probe pulse monitors the Raman scattering while the valence band is depleted, a decrease in the Raman intensity is observed corresponding to the decrease in the number of the upper-edge valence electrons. This is what was observed in the present experiment. The decay time, 45 ms in the present 2-nm microcrystallite sample, directly reflects the lifetime of the trap state D. The trap state is likely to be in the energy gap. This is inferred from the reported subpicosecond intraband relaxation above the energy gap.[20,21]

In the three-level model presented in Fig. 4, the photodynamics is simplified to include only three rate constants. In reality, however, it is more likely that D consists of a mani-

fold of states and that the upper edge of D has energy comparable to C so that an efficient nonradiative transfer is possible. The rate constant k_{cd} corresponds to this efficient nonradiative transfer. On the other hand, the rate constant k_{dv} reflects relaxation from the bottom edge of D, which has a low energy as implied by the observed slow decay constant. The manifold of states D is likely to be newly formed by photodarkening, though a small possibility cannot be ruled out that it is the opening of the decay channel and not the formation of a new state that is actually induced by the photodarkening effect.

We have presented unequivocal evidence for the existence of an efficient nonradiative decay channel to a long-lived trap state in a photodarkened CdS_xSe_{1-x}-doped glass. The lifetime of the trap state has been determined. The determined lifetime, 45 ms, is more than four orders of magnitude longer than the recently reported value (~ 1 μs) for CdSe quantum dots[22] and is characteristic of the photodarkening effect. We believe that the present study opens up many new directions of time-resolved Raman-spectroscopic studies on the photodarkening effect in semiconductor microcrystallites. The size dependence of the lifetime will give information on the nature of the trap state D. Measurements with higher time resolution will shed light on the branching between the direct recombination and the nonradiative transfer from the conduction band C. Of more general importance is the fact that we now have a practical means of controlling and monitoring the number of valence electrons in semiconductor microcrystallites. This "photocontrol of electrons" will enable us to study semiconductor microcrystallites having partially depleted valence bands with controlled population of electrons. The effect of quantum confinement on the level structure in semiconductor microcrystallites will thus be studied by time-resolved absorption spectroscopy. Nonlinear optical properties characteristic of the partially depleted valence band will also be of great interest from the viewpoint of applications. Studies in these lines will surely promote our understanding of the fundamental physics of semiconductor microcrystallites, including strong electron correlation effects that are not considered here.

*Author to whom correspondence should be addressed.

[1] P. D. Persans, An Tu, M. Lewis, T. Driscoll, and R. Redwing, in *Materials Issues in Microcrystalline Semiconductors*, edited by P. M. Fauchet, K. Tanaka, and C. C. Tsai, MRS Symposia Proceedings No. 164 (Materials Research Society, Pittsburgh, 1990), p. 105.

[2] N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, J. Appl. Phys. **61**, 5399 (1987).

[3] M. G. Bawendi, P. J. Carroll, W. L. Wilson, and L. E. Brus, J. Chem. Phys. **96**, 946 (1992).

[4] T. Miyoshi, Jpn. J. Appl. Phys. **31**, 375 (1992).

[5] P. Roussignol, D. Ricard, C. Flytzanis, and N. Neuroth, Phys. Rev. Lett. **62**, 312 (1989).

[6] M. C. Klein, F. Hache, D. Richard, and C. Flytzanis, Phys. Rev. B **42**, 11 123 (1990).

[7] J. J. Shiang, S. H. Risbud, and A. P. Alivisatos, J. Chem. Phys. **98**, 8432 (1993).

[8] L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).

[9] R. K. Jain and R. C. Lind, J. Opt. Soc. Am. **73**, 647 (1983).

[10] Junji Yumoto, Seiji Fukushima, and Ken-ichi Kubodera, Opt. Lett. **12**, 832 (1987).

[11] M. Tomita, T. Matsumoto, and M. Matsuoka, J. Opt. Soc. Am. B **6**, 165 (1989).

[12] P. Roussignol, D. Ricard, J. Lukasik, and C. Flytzanis, J. Opt. Soc. Am. B **4**, 5 (1987).

[13] M. Tomita and M. Matsuoka, J. Opt. Soc. Am. B **7**, 1198 (1990).

[14] B. Van Wonterghem, S. M. Saltiel, T. E. Dutton, and P. M. Rentzepis, J. Appl. Phys. **66**, 4935 (1989).

[15] P. Maly, F. Trojanek, and A. Svoboda, J. Opt. Soc. Am. B **10**, 1890 (1993).

[16] F. Hache, M. C. Clein, D. Ricard, and C. Flytzanis, J. Opt. Soc. Am. B **8**, 1802 (1991).

[17] J. Malhotra, D. J. Hagan, and B. G. Potter, J. Opt. Soc. Am. B **8**, 1531 (1991).

[18] M. Mitsunaga, H. Shinojima, and Ken-ichi Kubodera, J. Opt. Soc. Am. B **5**, 1448 (1988).

[19] S. Omi (private communication).

[20] M. C. Nuss, W. Zinth, and W. Kaiser, Appl. Phys. Lett. **49**, 1717 (1986).

[21] N. Peyghambarian, G. R. Olbright, and B. D. Fluegal, J. Opt. Soc. Am. B **3**, 248 (1986).

[22] D. J. Norris, A. Sacra, C. B. Murray, and M. G. Bawendi, Phys. Rev. Lett. **72**, 2612 (1994).