Room-temperature gain at 1.3 μm in PbS-doped glasses

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We report on room-temperature optical gain at the ground exciton transition of PbS quantum-dot-doped glasses while optical pumping into the next-higher exciton resonance. The material gain in the quantum dots is as large as 80 cm^{-1}. The dot-size selective excitation provides tunability of the optical gain. This is demonstrated by tuning the gain from 1317 to 1352 nm by changing the pump wavelength from 900 to 980 nm. © *1999 American Institute of Physics.* [S0003-6951(99)00146-1]

A major advantage of semiconductor-doped glasses over epitaxially grown structures is that glass is an inexpensive and robust material. Recent improvements in the manufacture of quantum dots (QDs) embedded in glassy matrices have resulted in structures with more uniform-size distribution; fewer vacancies, substitutional defects, and dangling bonds; higher dot concentration; and reduced photodarkening. As in epitaxially grown QD structures, the three-dimensional quantum-confinement effects in the incorporated semiconductor QDs allow for tailoring the linear and nonlinear optical properties of these materials. Thus, semiconductor quantum-dot-doped glasses are very promising candidate materials for photonics applications and may have niche applications relative to the complicated and expensive epitaxially grown structures.

In this letter, we report on room-temperature optical gain in PbS quantum-dot-doped glasses in the communication-wavelength region. When pumping into the first-excited exciton transition, optical gain is observed in the vicinity of the ground exciton resonance. We demonstrate that the spectral position of the peak gain can be changed from 1317 to 1352 nm by tuning the pump wavelength between 900 and 980 nm, a wavelength range which is accessible with InGaAs laser diodes. This tunability relies on the strong carrier confinement and the inhomogeneous broadening in the sample due to dot-size fluctuations, whereas the actual spectral width and position of the gain is given by the pump pulse.

In our experiments, we used PbS quantum-dot-doped glasses which were fabricated by a thermal treatment of an oxide molten glass.[1] In this method, the subsequent thermal treatment of the melted glasses precipitates the microcrystalline phase. PbS quantum-dot-doped glasses exhibit strong three-dimensional quantum-confinement effects at moderate nanocrystal size because of the large bulk exciton Bohr radius of $a_B \approx 18$ nm. This, combined with the small band-gap energy of 0.41 eV (room temperature) of PbS, allows for tuning the ground exciton absorption from the visible to 3 μm. Figure 1(a) shows the room-temperature absorption spectra of PbS-doped glasses fabricated with different thermal treatment schedules, which result in different average dot sizes. The strong quantum confinement in these structures is clearly observed in the large blueshift of the $1s$-absorption resonance with decreasing dot size. The appearance of defined subbanded peaks in all absorption spectra demonstrate the high quality of our samples and the relatively small size distribution of the PbS QDs. The average radii R of the QDs are deduced from fitting the spectral positions of the lowest-energy absorption peaks, which have been determined from the first derivative of the absorption spectra shown in Fig. 1(a), to the calculated $1s$-transition energies.[2] Here, we used the analytical hyperbolic band (HB) model,[3] which phenomenologically includes the nonparabolicity of the band structure and provides very good estimates for the $1s$-transition energies. Figure 1(b) compares the calculated dot-size-dependent energies of the $1s$ and $1p$ transition with the measured absorption maxima. As we can see, when the HB model is used to fit the $1s$-transition energy, the $1p$-transition energy is slightly underestimated.

To investigate the dynamics of the nonlinear absorption, we performed two-color pump–probe experiments. In these experiments, we used orthogonally polarized 130 fs pulses which are independently tunable in frequency. Pump and probe pulses are obtained from two optical parametric amplifiers, which are synchronously pumped by one regenerative Ti:sapphire amplifier at a repitition rate of 1 kHz. The zero time delay and the time resolution are given by the cross

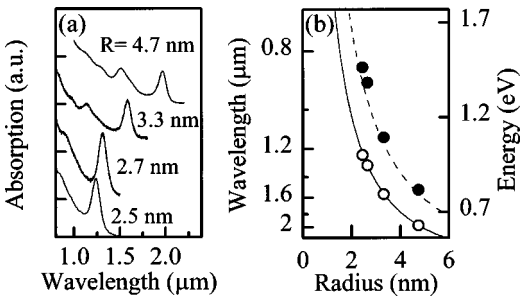

FIG. 1. (a) Room-temperature absorption spectra of PbS quantum-dot-doped glasses with different dot radii R. (b) Calculated $1s$- (solid line) and $1p$-transition (dashed line) energies; open (filled) circles; position of first (second) absorption peaks in (a).

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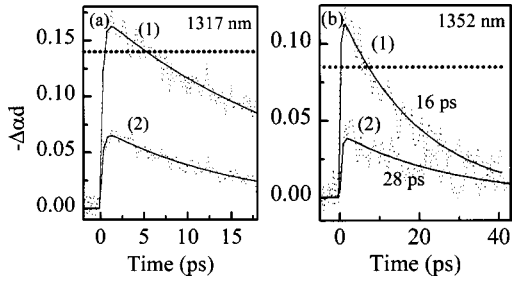

FIG. 2. Dynamics of the nonlinear absorption for the sample with $R=2.7$ nm, (a) probe at 1317 nm, which is at the $1s$-absorption peak, with a pump fluence of 4 mJ/cm^2 and pumping at 900 nm (1), which is at the $1p$-absorption peak, or pumping at 980 nm (2), which is on the low-energy side of the $1p$-absorption peak [see Fig. 3(a)]; (b) probe at 1352 nm and pump at 980 nm with pump fluences of 4 mJ/cm^2 (1) or 2 mJ/cm^2 (2). No gain is observed for probing at 1352 nm and pumping at 900 nm; the linear absorption is marked by the dotted horizontal lines.

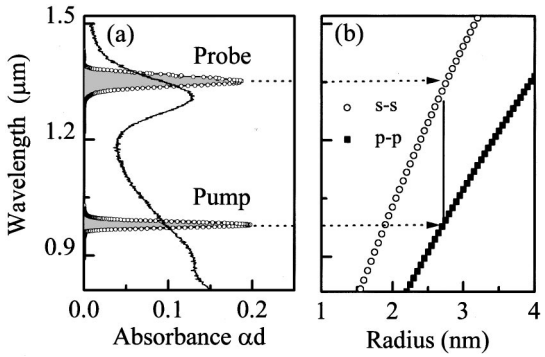

FIG. 3. (a) Absorption spectrum of the sample with $R=2.7$ nm and pump and probe pulses of Fig. 2(b). (b) Calculated $1s$- (open circles) and $1p$-transition (full squares) energies; the arrows mark the positions of pump and probe pulses as shown in (a).

correlation of both pulses, which has been measured to 200 fs. To minimize the fluctuation in the detected signal due to the laser-intensity noise, we utilized a dual-beam setup for the probe beam: one invariant reference path and one signal path that contains the sample. The signals of both (probe) beams are then detected with an autobalanced photoreceiver (Nirvana, New Focus), which cancels out signals that are common to both channels. With this technique, we are able to detect small transmission changes; however, the spectral resolution is limited by the pulse spectral width due to the spectral-integrated detection.

In the following, we concentrate on results obtained at the sample with an average dot radius of 2.7 nm. Figure 2 shows the dynamics of the nonlinear absorption for two different probe wavelengths: (a) resonant with and (b) 35 nm below the maximum of the $1s$-absorption peak. In Fig. 2(a) the pump wavelength is tuned and set either to the maximum of the $1p$-absorption resonance [curve (1)] or 80 nm below this maximum [curve (2)]. Fig. 2(b) shows the bleaching dynamics for two different pump intensities, whereas the pump wavelength is fixed at 80 nm below the maximum of the $1p$-absorption peak.

The dynamics of the bleaching signal can be fitted using a simple asymmetric response function with exponential rise and decay times (solid lines). All transients shown in Fig. 2 exhibit the same ultrafast rise time of about 300 fs, which is only slightly above the time resolution of our experiments. The recovery dynamics of the bleaching signal changes with the pump fluence, i.e., the decay time decreases with increasing pump fluence from 28 to 16 ps. The dotted horizontal lines in Fig. 2 mark the value of the linear absorption $\alpha_0 d$ at the respective probe wavelength.

The sub-ps buildup of the bleaching signal is consistent with previous observations of the ultrafast $1s$ dynamics in glass samples[4–6] and indicates that the phonon bottleneck[7] is not effective in this system. Note the large excess energy of the excited carriers, which varies with the pump–probe detuning between approximately 12 and 16 LO-phonon energies.[8] Different mechanisms have been proposed to overcome the phonon bottleneck.[9–12] Klimov and McBranch[4] showed that in a glass sample, the observed short rise time can be explained in terms of an Auger-like mechanism,[12] which involves confinement-enhanced energy transfer of the electron excess energy to a hole, with subsequent fast relaxation through its dense spectrum of states. The observed ps decay of the bleaching signal agrees well with the excitonic lifetime observed in various quantum-dot glass samples.[6,13–16] The origin of this fast and pump-fluence-dependent decay of the excitonic population has been discussed either in terms of carrier trapping effects,[14–16] i.e., at surface located defects, or Auger recombination.[17–19]

Optical gain is observed when the negative nonlinear absorption exceeds the linear absorption (dotted horizontal lines in Fig. 2). The buildup time of the gain, as seen in each curve (1) in Figs. 2(a) and 2(b), is about 500 fs and the gain lasts for 5–6 ps. The maximum gain value is $gd=-(\alpha_0+\Delta\alpha)\,d\approx 0.022$, which corresponds to 15% (a) and 28% (b) of the linear absorption. From the measured optical gain and the filling factor (0.15%) of the QDs in the glassy material, we estimate a material gain in the QDs of 80 cm^{-1}. This room-temperature material gain is large compared to earlier results of 33 cm^{-1} obtained by Butty *et al.*[20] in sol–gel-derived CdS QDs. The significant enhancement of the optical gain can be attributed to the stronger three-dimensional quantum confinement in our samples, which is expected to enhance the optical nonlinearities.[21] The difference in the quantum confinement can be seen if we compare the normalized dot radius $R/a_B=1.3$ for the sample used in Ref. 20 to $R/a_B=0.15$ in the PbS quantum-dot-doped glass used in the experiments presented here.

In Fig. 3, we illustrate the spectral dependence of the optical gain. Here, the spectral positions of the pump and probe pulses, as used in the experiments of Fig. 2(b), are compared to the linear absorption of the sample [Fig. 3(a)] and the calculated $1s-1p$ splitting [Fig. 3(b)]. When pumping into the $1p$-absorption resonance, optical gain is found only when the pump–probe detuning is close or equal to the $1s-1p$ splitting for a given dot size. More explicitly, gain is found only for pumping at 900 nm and probing at 1317 nm [see curve (1) of Fig. 2(a)] or for pumping at 980 nm and probing at 1352 nm [see curve (1) of Fig. 2(b)]. However, no gain is observed for pumping at 980 nm and probing at 1317 nm [see curve (2) of Fig. 2(a)] or for pumping at 900 nm and probing at 1352 nm. Since in our experiments, the inhomogeneous broadening of the $1p$ absorption is large compared to the spectral width of the pump pulse, the pump pulse only excites a small portion of all QDs for which the pump pulse

is resonant with the $1p$ transition. Optical gain is only possible in this subset of pump-pulse-selected QDs and will appear around the transition frequencies between the lowest confined electron and hole levels after relaxation of the excited electron–hole pairs to the exciton ground state. In this case, taking into account our dot-size-selective excitation, as the mismatch between the $1s-1p$ splitting and the pump–probe detuning increases, the ratio between gain from the excited QDs and absorption from the nonexcited QDs decreases. Consequently, the effective optical gain disappears if this mismatch is too large, as demonstrated in curve (2) in Fig. 2(a). Here, the detuning of the probe pulse from the maximum gain position is about 35 nm, which corresponds to the initial spectral distribution of the excited carriers given by the pump pulse.

So far, we neglected the Coulomb and spin-orbit interactions, which change the selection rules and, therefore, increase the number of dipole-allowed transitions.[22] These additional transitions give rise to optical gain at new frequencies. For example, Hu *et al.*[23] used a microscopic model to describe optical gain observed in CdS and CdSe QDs.[20,24] Here, the gain was spectrally broad and located on the low-energy side of the ground exciton absorption. This was explained by taking into account one and two electron–hole pair recombination, i.e., excitons and biexcitons. On the basis of these results, we would expect maximum gain at a pump–probe detuning slightly larger than the $1s-1p$ splitting when pumping into the $1p$ transition. Our limited spectral resolution and accuracy of the HB model to calculate the $1p$-transition energies does not allow a final conclusion whether or not a shift or increased gain bandwidth due to the biexcitonic contributions is present. Furthermore, our pronounced dot-size-dependent selective excitation prohibits a direct comparison of our experimental results and the earlier experiments on CdS and CdSe QDs.

In summary, PbS quantum-dot-doped glasses show room-temperature gain of 80 cm^{-1} in the communication wavelength region around 1.3 μm. We have shown that we can utilize the strong quantum-confinement effect and the inhomogeneous broadening due to dot-size fluctuations to tune the gain spectrum of an individual PbS-doped glass. Furthermore, because the exciton ground-state transitions, where the gain is observed, can be widely tuned by changing the size of the QDs, we believe that room-temperature optical gain in PbS quantum-dot-doped glasses is possible over a wide spectral range. This gain tunability together with the demonstrated possibility of optical pumping at the wavelength of commercially available laser diodes shows that PbS quantum-dot-doped glasses may be suitable low-cost alternatives to current amplifiers and lasers for optical communication applications.

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