Photodarkening effect and the optical nonlinearity in a quantum-confined, semiconductor-doped glass

P. Horan and W. Blau

Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland

The room-temperature optical nonlinear behavior of a quantum-confined CdSe-doped glass with ~25-Å-size particles is examined. The photodarkening effect is found to be important in this glass. The effect and its influence on the nonlinear response of the glass is investigated experimentally through the use of optical absorption saturation and forward-degenerate four-wave-mixing methods.

INTRODUCTION

Spatial confinement of excitons or free carriers in one or more dimensions has recently attracted considerable interest owing to the fascinating fundamental physics involved and also owing to its potential applications at room temperature in nonlinear-optical devices [for an introduction see Ref. 1]. Three-dimensional confinement, also termed quantum-dot, systems can indeed be observed in microcrystalline semiconductor samples with crystallite sizes in the 20–80-Å range for II–VI compounds.[2,3] The optical properties of such quantum dots differ substantially from those of the bulk material, with a blue shift of the optical absorption and a simultaneous increase in oscillator strength with decreasing particle size, described by particle-in-a-box behavior. Theoretical treatment of the nonlinear-optical properties of quantum dots predicts a significant resonant third-order nonlinearity due to saturation of these transitions.[4,5]

Semiconductor-doped glass, containing nanometer-size CdS_xSe_{1-x} microcrystallites, has attracted much attention. Commercially available sharp cutoff filters manufactured from these materials contain microcrystallites in the 8–12-nm range, and although they show a sizable nonlinear response, no evidence of size quantization has been observed.[6] Careful control of the fabrication process, however, can produce particles in the 2–8-nm range that show clear evidence of size quantization.[6,7] In the commercial, large crystallite glasses, a photochemical darkening effect is seen, which causes a slight discoloration of the glass and a sizable change in excited-state population dynamics.[8] Studies to date of the smaller crystallite glasses have been carried out at low temperatures, where photodarkening effects are considerably reduced. We have carried out room-temperature-transmission and four-wave-mixing experiments to examine the influence of the photodarkening effect on the nonlinear response of one quantum-confined CdSe-doped glass.

LINEAR SPECTROSCOPY OF THE SAMPLE

The sample studied was a borosilicate glass doped with CdSe microcrystallites (thickness 0.27 mm) provided by D. W Hall, Corning Glassworks (Corning 203 AME). By heat treatment of the formed glass at 600°C, microcrystallites grow by the process of Ostwald ripening[3] and give an intense orange coloring of the sample owing to the appearance of an absorption peak centered at 546 nm (see Fig. 1). From the comparison of the position of this peak with the particle-in-a-box model, and by using the bulk effective masses, a microcrystallite size of ~25 Å can be deduced. Since the bulk-exciton radius for CdSe is ~45 Å,[9] this particle size corresponds to moderate confinement as described by Efros and Efros.[10] A bound on the particle-size distribution can be estimated by assuming it to be the sole broadening mechanism (which it is not) and an initial delta function. This gives a size distribution of 25 ± 3 Å, which is equivalent to an uncertainty of just one atomic layer. A phonon-broadening contribution may be observed in the low-temperature (12-K) absorption spectrum. Along with the typical blue shift of the peak, the HWHM is seen to narrow from 23 to 19 nm. The phonon contribution has been discussed in greater detail by Roussignol *et al.*[11]

Photoluminescence spectra were taken by using the 488-nm line of a cw argon laser. At room temperature we observe a sharp feature at 580 nm. With suitable scaling this can be shown to lie in the low-energy tail of the absorption band and is thus assigned to direct recombination. The observed Stokes shift of ~50 nm is typical for an inhomogenously broadened system with spectral cross relaxation faster than the observation time (much less than microsecond range). Similar shifts are commonly observed and are well known in laser dyes where the recombination occurs between rovibronic states of the S_1 and S_0 levels, with spectral cross relaxation occurring on a femtosecond time scale.[12] A broad feature, centered at 750 nm, is also observed, although it is not shown in Fig. 1. Similar broad features are observed in commercially available CdS_xSe_{1-x}-doped glass filters.[13] In the commercial glasses this broad peak has been shown to be associated with the photodarkening effect.[8]

OPTICAL-SATURATION MEASUREMENTS

Schmitt-Rink *et al.*[4] have shown that the nonlinear-optical response of a semiconductor quantum dot will be characterized only by state filling, because band filling, bandgap renormalization, and exciton screening cannot be observed in
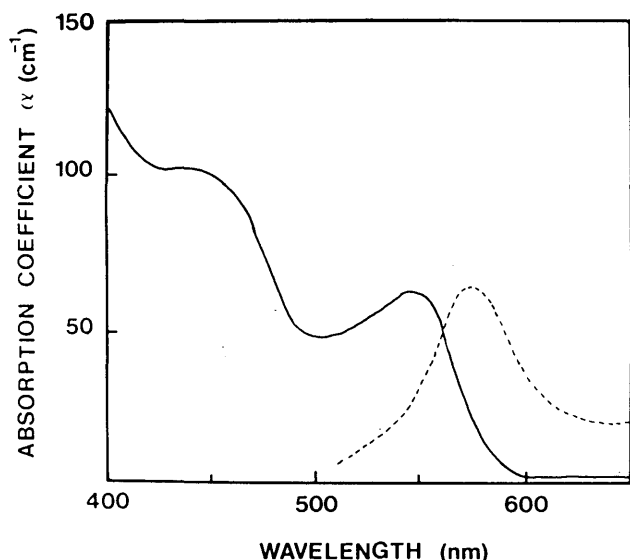
Fig. 1. Room-temperature absorption and photoluminescence spectra of Corning experimental glass AME 203.

such systems. This means that the third-order nonlinear-optical response will be based on saturation of the discrete transition.

All nonlinear-optical experiments were performed with a high-resolution dye laser (PRA LN 107) pumped by a high-pressure nitrogen laser (PRA LN 1000). Tunable pulses of 500-psec pulse width and 0.5-Å spectral bandwidth were obtained at a 3-Hz repetition rate and a typical energy of 30 μJ at the sample, which when focused to a spot of approximately 150-μm radius yielded a maximum laser fluence of 20 mJ/cm^2 and a peak intensity of 4×10^7 W/cm^2.

Figure 2 shows the intensity dependence of the transmission of a single dye-laser pulse at 546 nm through the sample. Saturable absorption is clearly observed. An ideal quantum dot should behave as a simple two-level system, with a ground state and an excited state and transitions only between these two levels. Such a simple two-level system should saturate completely.[13] This clearly is not the case.

The limited saturation observed could be accounted for by a three-level model with rapid scattering from the highest energy state. Such a model has been proposed for the larger, nonconfined, doped glasses.[14] From photoluminescence data they produced a model of a conduction and valence band and an intermediate, long-lived trapping level associated with the broad band near 750 nm observed in luminescence spectra. In the confined glasses the conduction band would be replaced by the quantized levels, and the trapping states appear to be similar. The rapid (picosecond) scattering from the conduction band to the trap level should be enhanced in the confined glass, where increased coupling to short-wavelength optical phonons has been predicted.[4]

The situation is further complicated by the photodarkening effect, which greatly reduces the excited-state lifetime.[8] In these measurements the sample has been well exposed and is in the darkened (aged) state. Morgan et al.[15] report that complete saturation could be achieved only before the onset of darkening, even at 10 K. In contrast, Hall and Borrelli[16] observe almost no saturation in a similar sample in which picosecond excitation is used at room temperature.

The variety of results illustrates the complex interplay among the excitation time scale, energy, and the state of photodarkening.

WAVE-MIXING EXPERIMENTS

In order to determine the magnitude and intensity dependence of the nonlinearity directly, we have carried out laser-induced grating (LIG) experiments (also termed degenerate forward four-wave mixing). The experimental setup is described in Ref. 17. The laser beam was split into parallel beams of equal magnitude that were focused into the sample through a 30-cm focal-length lens. These two pump pulses interfere in the sample and set up a laser-induced grating through the optical nonlinearity. Simultaneously, part of the same pump pulse is diffracted off this grating. The measurement of the peak diffraction efficiency η gives $\chi^{(3)}$ directly. The magnitude of the nonlinearity is given by[17]

$$\chi^{(3)} = \frac{8c^2 n^2 \epsilon_0 \alpha \sqrt{\eta}}{3\omega I(1-T)}, \tag{1}$$

where I is the peak intensity of one pulse, T is the sample transmission, α is the absorption at frequency ω, and n is the refractive index. The angle between the two pumps was kept small (<2 deg) such that the thin grating condition should prevail.[17] It should be noted that the intensity dependence of η should be quadratic, and that the diffracted signal should depend cubically on I, if $|\chi^{(3)}|$ is a material constant. Initial measurements soon revealed the quick and effective formation of a permanent grating in the glass, which considerably altered the nonlinear response. Be-
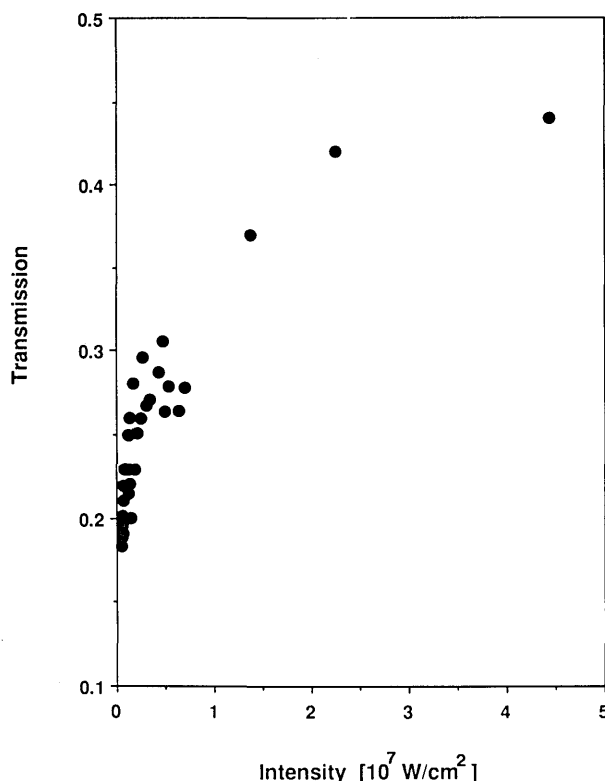

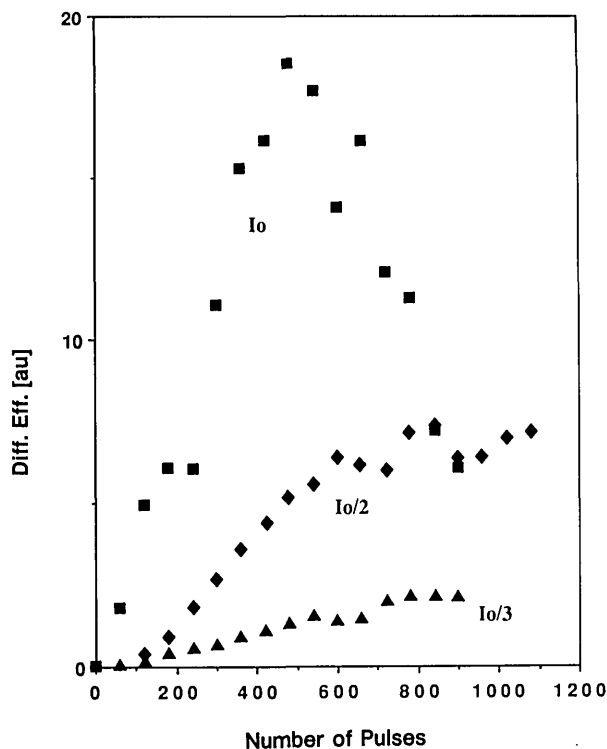Fig. 2. Intensity dependence of the sample transmission at λ = 546 nm.

Fig. 3.   Initial diffraction efficiency from the permanent grating, where $I_0 = 2 \times 10^7$ W/cm^2.
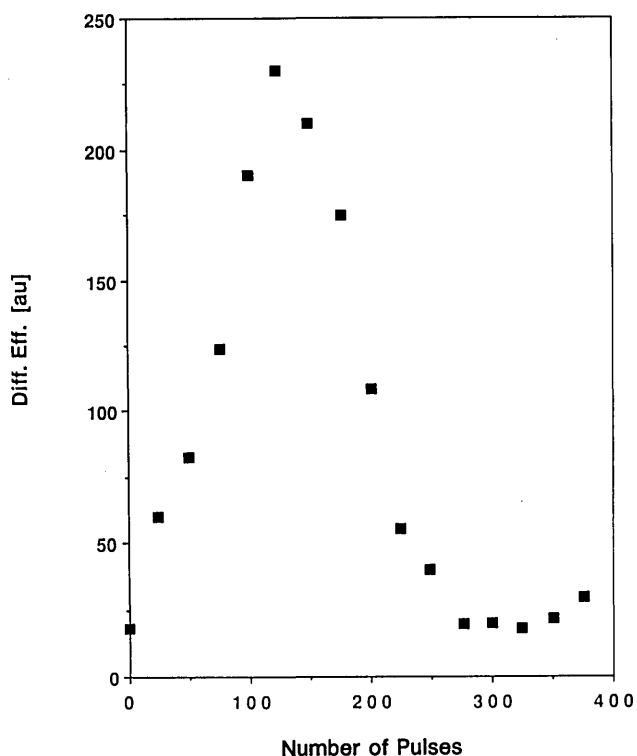

Fig. 4.   Diffraction efficiency from the permanent grating showing a full cycle.

cause of the obvious influence in this glass, the darkening effect was investigated first.

Darkening Effect

The formation of a permanent grating could be observed by first exposing the glass to two interfering beams, as in the usual arrangement for laser-induced grating measurements. One of the beams is then blocked. For a true transient grating no diffraction should then be observed, but diffraction may still occur from a permanent grating. The term permanent is used in the sense that, barring further exposure, the photochemical change is permanent and can be read out at a later time (2 days was the maximum that alignment was maintained in our case). To measure the buildup of the grating, the glass was exposed to a set number of pulses, i.e., 20 or 50. One beam was then blocked, and the beam diffracted to the first order from the permanent grating was measured. This procedure was repeated many times to follow the evolution of the permanent grating. For all these experiments the laser was operated at 1 Hz.

Starting from a fresh area of glass the initial buildup of the permanent grating was measured at intervals of 20 pulses. The laser was operated at the peak of the absorption at 546 nm, and the intensity was kept constant to within a few percent. After an initial period of a few tens of shots, the development of the grating is essentially linear. This linear behavior continues for several hundred shots until the diffraction efficiency reaches a maximum and then decreases. Figure 3 shows the buildup of the grating at three different intensities, where $I_0 = 2 \times 10^7$ W/cm^2. From these results the effect does not appear to depend only on the energy deposited but to be more efficient at higher intensities.

Figure 4 shows an entire cycle of the permanent grating. Such behavior is in agreement with the observations of the darkening effect in the commercial semiconductor-doped glass filters. Roussignol et al.[8] observe the creation of a permanent grating and, furthermore, that the grating may equally well be erased by a laser beam. These researchers postulate that the sites involved in forming the permanent grating may be cycled only once, i.e., a site may darken and then clear only once and thereafter be unavailable.

As has been mentioned, the darkening effect is attributed to some form of electron trapping, either at real defects or at surface states. The greatly increased prominence of the effect in this quantum-confined glass as compared with the commercial glass filters would be expected if the trapping states were associated with the surface. In the quantum-confined glass, the reduced particle size means a much greater surface-to-volume ratio, and so the proportion of surface trapping states should be much greater.

Since this is an electronic effect, it may be expected to have some bearing on the nonlinear response. This was investigated by measuring the average total energy diffracted to the first order over 50 pulses, stopping to measure the permanent grating, and repeating the procedure over the evolution of the permanent grating. By subtracting the permanent grating contribution from the total, the transient grating response could be monitored. Results are plotted in Fig. 5. At the bottom is the diffraction from the permanent grating, measured every 50 shots. Above is plotted the average signal from the transient grating for every set of 50 shots,
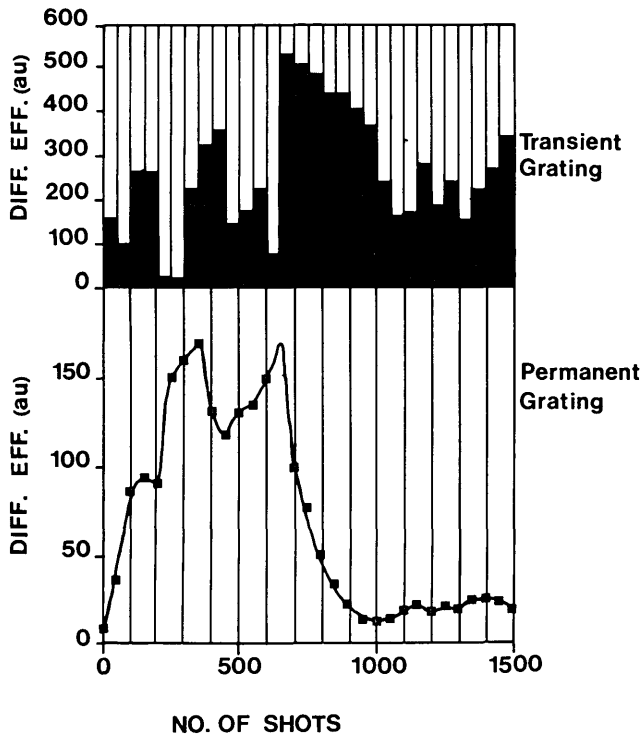
Fig. 5. Self-diffraction experiments from a laser-induced grating. The diffraction efficiency from the permanent grating and the transient grating is measured and displayed simultaneously.

both sets of data being plotted on the same arbitrary scale. The uneven development of the permanent grating in this particular case was chosen to further illustrate the general behavior.

The permanent grating evolves in a somewhat erratic manner but follows the general trend outlined above. The accompanying transient grating measurements appear almost random, but a general correlation may be made. When the two graphs are compared, a low transient grating signal is obtained whenever the permanent grating is increasing. Similarly, the response of the transient grating is greatly enhanced when the permanent grating is decreasing. Such behavior supports the idea that the permanent grating is associated with electron trapping. When the permanent grating is improving, electrons are being trapped and so are not available to saturate the transition. Decrease of the permanent grating results in trapped electrons' being freed and thus available to enhance the transient response. Even when the permanent grating has evolved to the residual stage, small changes in the permanent grating are reflected in large changes in the transient response. This behavior is observed to continue even after many thousands of shots. Any quantitative study of this effect would require a knowledge of the particle density, but the sample used is visibly unevenly doped. To further investigate the nonlinear response, the intensity dependence of the diffraction was measured.

Intensity Dependence of the Laser-Induced Grating Response

The intensity dependence of the diffracted beam should be cubic for a third-order process such as this. The usual LIG

arrangement was used, the laser input intensity being reduced with neutral-density filters. The intensity dependence was measured during the initial buildup of the permanent grating and again once the permanent grating had evolved to the long-term stable state. During operation with a fresh area of glass, and within the first hundred shots, the intensity dependence of the total diffracted intensity signal was measured. To minimize the influence of the permanent grating, the measurements were made at the lowest intensity first and then at increased intensities. With these precautions, and during operation with a fresh area of glass, the contribution to the total diffracted signal from the permanent grating is negligible and may be ignored. Thus the measured signal is derived only from a transient grating. The measurements are noisy, as may be expected, since an average of only four shots was taken for each point.

The results are plotted in log–log form in Fig. 6(a). The data are fitted to a line with a slope of 0.5, much less than the expected 3. This less than linear dependence may again be attributed to the participation of electrons in the formation of the permanent grating. From Fig. 5 it is seen how the transient grating is greatly reduced when the permanent grating is increasing.

After the initial behavior was investigated, the permanent grating was allowed to evolve through to the residual stable
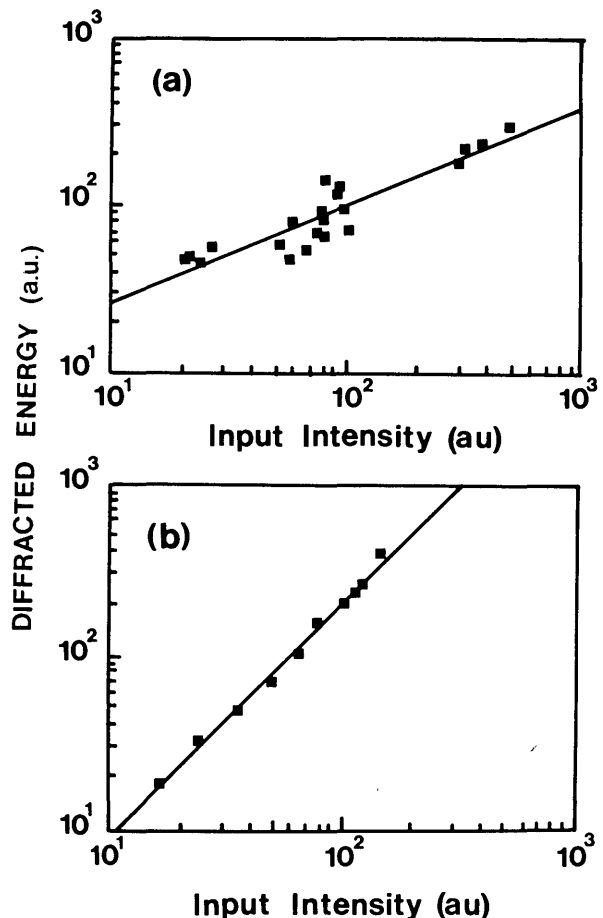

Fig. 6. Intensity dependence of the diffracted signal (a) during the initial formation of the permanent grating and (b) for an aged glass.

stage, and the intensity dependence again was measured over the same intensity range. The total diffracted intensity is measured, but in this regime the contribution from the permanent grating is very small, typically less than 10%, and so was neglected. Thus the signal measured is, essentially, again due only to the transient grating. The intensity was reduced to the point where the transient response approached that of the residual permanent grating. While always showing a definite power dependence, the power was not observed to be constant but varied quite considerably. On a log–log plot, slopes of 1.3–1.6 have been observed, but slopes as low as 0.9 have also been observed. Typical results are plotted in Fig. 6(b), where a line with a slope of 1.34 is fitted to the particular data.

The variations in response may arise from small differences in the state of the permanent grating. It can be seen from Fig. 5 how small variations in the permanent grating result in large changes in the transient grating response. Also, as each measurement was taken at a different point on the sample, local variations in particle density (which there are) may be the cause. Whatever the cause of the variations, it should be noted that the dependence is still much less than the expected cubic. Such behavior often indicates saturation of a transition, but in this case lower intensities could not be used, as the signal became lost in the noise from the residual permanent grating. Such considerations aside, the considerable difference observed between the fresh and aged glass is in agreement with the comments made earlier on the transient nonlinear response.

Disregarding the difficulties, an effective third-order susceptibility may still be computed. For the particular data presented in Fig. 6(b), a maximum diffraction efficiency of 3 $\times$ 10^{-3} was measured for an input intensity of 1.9 $\times$ 10^7 W/cm^2 at 546 nm. When Eq. (1) is used, this gives $\chi^{(3)}_{eff} = 3 \times 10^{-10}$ esu. Equally, when the lowest data point is used, a larger value of $\chi^{(3)} = 2 \times 10^{-9}$ esu may be calculated, the difference arising from the fact that the graph is not cubic. This is not a significant improvement compared with results for the nonconfined glasses measured with the same technique and laser.[17] In fact, a more reasonable figure of comparison is $\chi^{(3)}/\alpha$, in which case they are approximately equal. Obviously the measured quantity is an effective nonlinearity and thus depends on the laser-pulse duration. Comparison with the results obtained with different lasers has to take this into account.

CONCLUSIONS

The semiconductor particles in this glass exhibit quantum-confinement effects and can be classed as a quantum-dot system. The nonlinear response is found to be strongly influenced by the photodarkening effect and is sensitive to the particular state of the photodarkening cycle. The measured magnitude of the nonlinearity is not greatly enhanced compared with that for nonconfined samples.

ACKNOWLEDGMENTS

REFERENCES

1. P. Horan and W. Blau, Contemp. Phys. **28,** 59 (1987); D. S. Chemla and D. A. B. Miller, J. Opt. Soc. Am. B **2,** 1155 (1985).
2. L. Brus, J. Phys. Chem. **90,** 2555 (1986).
3. N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, J. Appl. Phys. **61,** 5399 (1987).
4. S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, Phys. Rev. B **35,** 8113 (1987).
5. E. Hanamura, Phys. Rev. B **35,** 1273 (1988).
6. N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, J. Appl. Phys. **61,** 5399 (1987).
7. A. I. Ekimov and A. A. Onushchenko, JETP Lett. **40,** 1137 (1984).
8. P. Roussignol, D. Ricard, J. Lukasik, and C. Flytzanis, J. Opt. Soc. Am. B **4,** 5 (1987).
9. E. Cohen and M. D. Sturge, Phys. Rev. B **25,** 3828 (1982).
10. Al. L. Efros and A. L. Efros, Sov. Phys. Semicond. **16,** 772 (1982).
11. P. Roussignol, D. Ricard, and C. Flytzanis, Phys. Rev. Lett. **62,** 312 (1989).
12. W. Demtröder, *Laser Spectroscopy* (Springer-Verlag, Berlin, 1982).
13. J. Warnock and D. D. Awschalom, Phys. Rev. B **32,** 5529 (1985).
14. M. Tomita, T. Matsumoto, and M. Matsuoka, J. Opt. Soc. Am. B. **6,** 165, (1989).
15. R. A. Morgan, S. H. Park, S. W. Koch, and N. Peyghambarian, in *Digest of Topical Meeting on Quantum Wells for Optics and Optoelectronics* (Optical Society of America, Washington, D.C., 1989).
16. D. W. Hall and N. F. Borrelli, J. Opt. Soc. Am. B **5,** 1650 (1988).
17. P. Horan and W. Blau, Semicond. Sci. Technol. **2,** 382 (1987).