Femtosecond relaxation excited carriers in microscopic $CdSe_xS_{1-x}$ crystallites in a glassy matrix at a high excitation intensity

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The relaxation time of carriers excited in microscopic selenium–cadmium crystallites by a laser pulse with an intensity of 10^{10}–10^{11} W/cm^2 has been found to be shorter than 30 fs. Analysis of the experimental data shows that the primary mechanisms by which the excited carriers relax are carrier–carrier scattering and Auger recombination.

Methods of femtosecond laser spectroscopy have recently been used actively to study the relaxation of excited carriers in semiconductors.[1,2] Glasses doped with microscopic $CdSe_xS_{1-x}$ crystallites have been of particular interest. This readily available material has a very large nonlinear susceptibility and a short response time and thus holds promise for use in optoelectronics. The dimensions of the microscopic crystallites in commercial glass samples are on the order of 100 Å, and their concentration is $\sim 10^{15}$ cm^{-3}. It was shown in Refs. 1 and 3 that at an excited-carrier density

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N below 10^{18} cm^{-3} the primary mechanism for the intraband relaxation in these glasses is a scattering of excited carriers by optical phonons with a time scale of 200–500 fs, while the interband recombination time is measured in tens of picoseconds. In this letter we are reporting a study of the relaxation of excited carriers in RC-8 Schott commercial filters at much higher densities, at which the intensity of the femtosecond exciting pulse is close to the threshold for damage.

A test sample 400 μm thick was excited by a 300-fs pulse at a wavelength of 612 nm(200 meV above the bottom of the conduction band). The excitation intensity I could be varied over the range 10^{10}–10^{13} W/cm^2 by means of neutral filters and a change in focusing. The optical density of the sample at the excitation wavelength was ~ 1. To study the time evolution of the absorption by the sample, we probed the excitation region with a wide-band (continuum) femtosecond pulse, which was delayed with respect to the exciting pulse.[4] The intensity of the probe pulse did not exceed 10^9 W/cm^2. Using a multichannel optical analyzer connected to a computer, we measured the spectra of the excited sample and of an unexcited sample in the spectral interval 600–720 nm, which contains the interval from the excitation level to the bottom of the band. The delay of the probe pulse was varied. Difference spectra were calculated. In some of the experiments, the relative delay of the various spectral components of the probe pulse was determined with the help of a wide-band dye; it was found to be 13 fs/nm. The short-wavelength components had a shorter delay. To determine the number of photons of the exciting pulse which were absorbed in the sample, we carried out an additional experiment, in which the energy incident on the sample and that transmitted through it were measured simultaneously (the reflection did not exceed 4%). All the experiments were carried out at room temperature.

Figure 1 shows the optical density of the sample as a function of the intensity of the exciting pulse, I. The sample is seen to be bleached almost completely at 10^{12} W/cm^2. The absorption then increases, and the sample suffers damage at 10^{13} W/cm^2. Figure 2 shows difference spectra recorded at $I = 10^{10}$–10^{11} W/cm^2 for a delay of 3 ps. The observed shift of the bleaching peak toward shorter wavelengths and the broadening of the bleaching band are due to a filling of bands by carriers (a Burshteĭn–Moss shift). When the delay of the various spectral components of the probe pulse is taken into account, it is found that the time evolution of the bleaching is the same at all wavelengths. The leading edge corresponds to the integral of the correlation function

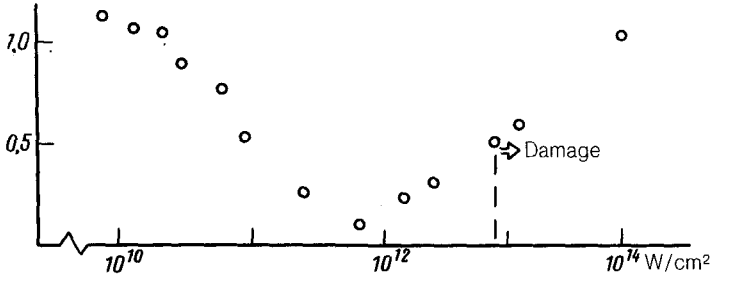

FIG. 1. Optical density of a sample for exciting pulses of various intensities.

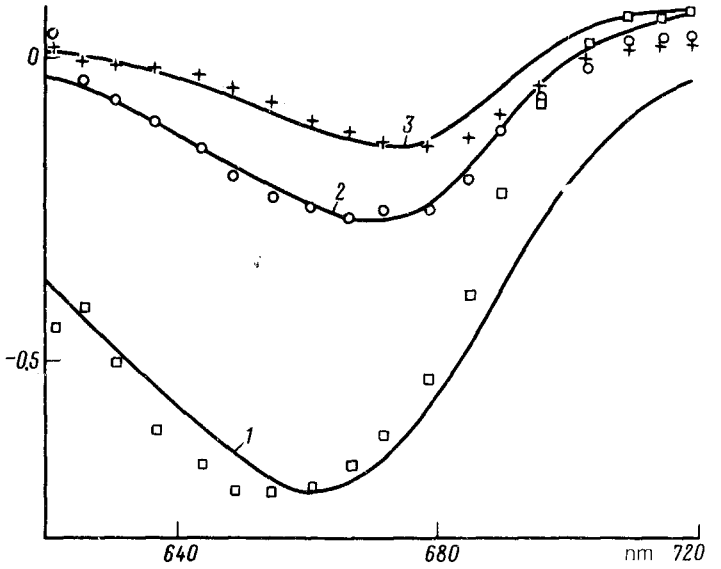

FIG. 2. Experimental and theoretical difference spectra. The intensity I (in units of 10^{10} W/cm^2): □—9; ○—1.8; +—1.2. N (units of 10^{18} cm^{-3}): *1*—18.5; *2*—7.5; *3*—4.5.

of the exciting and probe pulses; thereafter, the magnitude of the bleaching remains the same up to a delay of 40 ps. It follows that the relaxation time of the excited carriers at the band bottom does not exceed 10^{-13} s, while the interband recombination time is greater than 500 ps at the least. The time scale of the transitions of the excited carriers from the excitation level, τ, was estimated by the method of Ref. 5 from the magnitude of the bleaching time at 612 nm for the lowest intensity (10^{10} W/cm^2). It can be seen from Fig. 2 that the bleaching at the excitation wavelength does not exceed the noise level. On the other hand, the density of absorbed photons at this intensity is 10^{20} cm^{-3}, so in the absence of a relaxation the bleaching of the sample at the excitation wavelength would be complete. A comparison of these values yields an upper estimate $\tau < 30$ fs on the relaxation time; this estimate is much shorter than the times observed at I values up to 10^9 W/cm^2 (Ref. 3).

Difference spectra were calculated for a sample at a delay of 3 ps; the dependence of the exchange-correlation shift[6] and that of the rate of intraband relaxation, which determines the width of the absorption line, on the charged-particle density N were taken into account. The best agreement with the experimental spectra is found at values of N more than an order of magnitude lower than the density of absorbed photons found from Fig. 1 at $I = 10^{11}$ W/cm^2, for example, the best agreement is found at $N = 2\times10^{19}$ cm^{-3} (Fig. 2), although it can be concluded from Fig. 1 that the density of absorbed photons at this intensity is 5×10^{20} cm^{-3} (a calculation based on the absorption spectrum of the sample puts the fraction by volume of the microscopic crystallites at 3.3×10^{-3}). Two-photon absorption can be ignored[7] at $I < 10^{11}$ W/cm^2, so the only way to explain the discrepancy is to assume that a recombination

of the particles occurs over a time < 1 ps. We suggest that the recombination results from Auger processes, although doubt that such processes play a role in microscopic crystallites in glass has recently been expressed.[1] The sharp increase in the rate of Auger recombination at the time at which the pulse passes is a consequence of a rapid increase in N and the high carrier temperature, because the frequency of the exciting pulse is about 200 meV greater than the band gap. After the pump pulse has passed, Auger processes should cease over a time of less than a picosecond, because of the rapid carrier cooling (over a time scale of 200–500 fs). A comparison of the theoretical and experimental difference spectra yields an estimate of the relaxation rate. For $I = 10^{10}$ W/cm^2 we find a time $\tau = 30$ fs, which agrees with the estimate found from the magnitude of the bleaching at 612 nm.

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