Femtosecond carrier relaxation in semiconductor-doped glasses

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Light induced changes of absorption in semiconductor-doped glasses are studied on the femtosecond and picosecond time scale. Extremely rapid absorption recovery times of 200 fs are found when carriers are excited with large excess energy (500 meV) above the absorption edge of the semiconductor-doped glasses. Excitation close to the band edge results in a slower absorption recovery with a time constant of $\tau \simeq 100$ ps.

Semiconductor-doped glasses, being well known as low pass optical filters, have attracted considerable attention during the past few years. These glasses incorporate small microcrystallites of ~ 100–1000 Å diameter and show extremely interesting optical properties due to dielectric[1–4] and electronic[5] confinement. Strong nonlinear absorption was observed[1] and significant enhancement of the third-order nonlinear optical susceptibility χ^3 compared to the corresponding crystalline semiconductors was reported.[2,3] Values of χ^3 as large as 1.3×10^{-8} esu at 532 nm were measured in Ref. 2. Recently, the nonlinear index of refraction, n_2, of a semiconductor-doped glass was determined in the vicinity of the absorption edge.[4] The large optical nonlinearities are attributed to the generation of an electron-hole plasma in the semiconductor crystallites. Local field effects arising from dielectric confinement in the small particles are responsible for the enhanced optical nonlinearities.[2,3,9] In this letter we report on femtosecond absorption studies of several semiconductor-doped glasses. Very fast absorption changes and absorption recovery times of 200 fs are observed when electrons are optically excited into the conduction band with excess energies of more than 100 meV. Our data for different excitation energies show evidence for carrier density dependent band filling processes different from bulk semiconductors.

Semiconductor-doped glasses are produced by adding a few percent of cadmium, sulfur, selenium, tellurium, and their compounds to the glass melt. Annealing at temperatures between 500 and 700 °C then leads to intensely colored glass samples.[6–8] Chemical analysis, optical techniques, x-ray diffraction, and electron microscopy have demonstrated that the semiconductor inclusions are microcrystallites of composition $CdS_x Se_{1-x}$ or $CdSe_x Te_{1-x}$ in the size regime of less than one hundred to several hundred Å.[2,6–8] In Fig. 1 the absorption spectra of three samples are depicted. Specimens 1 to 3 correspond to the commercial glass filters Schott RG 830, RG 715, and RG 645, respectively. The three samples show very similar absorption curves. An absorption edge is followed by an absorption plateau for photon energies much higher than the band gap. We find that the absorption edge is almost a factor of 3 less steep for the crystallites embedded in the glass matrix compared to the bulk material. The difference is probably due to inhomogeneities in the small crystallites, to surface effects at the interface between the semiconductor and the glass matrix or due to the confinement of the carriers in the small crystallites.

Disregarding any possible quantum effects due to electronic confinement, the absorption of the semiconductor-doped glasses can be described in the framework of the Maxwell–Garnett theory of composite materials.[9] Small spherical inclusions ($r < \lambda$) of an absorption coefficient α_1 and a refractive index n_1 (or dielectric constant $\epsilon_1 = \epsilon_1' + \epsilon_1''$) are incorporated in a transparent glass matrix with a dielectric constant ϵ_2. If the inclusions occupy a fractional volume $p \ll 1$, the absorption coefficient α_c of the composite system (refractive index n_c) has the form[9]

$$\alpha_c = p \frac{n_1}{n_c} \frac{9\epsilon_2^2}{(\epsilon_1' + 2\epsilon_2)^2 + \epsilon_1''^2} = \gamma \alpha_1. \qquad (1)$$

According to Eq. (1), α_c is proportional to the absorption coefficient α_1 of the semiconductor inclusions. Only in the spectral range of the band edge is the proportionality factor γ
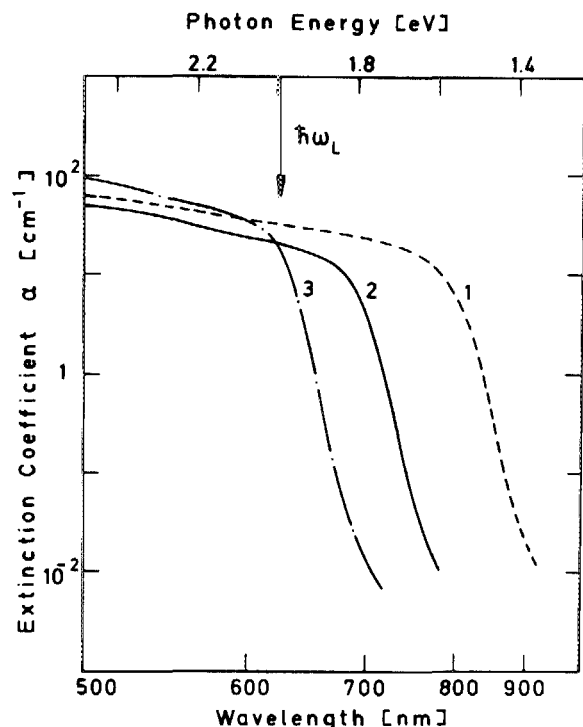

FIG. 1. Absorbance spectrum of the three investigated semiconductor-doped glass samples. The wavelength of the femtosecond light pulses is indicated by an arrow.

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strongly frequency dependent. The filling factor p can be deduced from Eq. (1) by comparing the absorption coefficient of the glasses and the corresponding crystalline semiconductors. At the absorption plateau the absorption coefficient $\alpha_1 = 6 \times 10^4$ cm^{-1} of CdS$_x$Se$_{1-x}$ crystals corresponds to $\alpha_c \simeq 100$ cm^{-1} of the composite system. With $n_1 = 2.5$, $n_c = 1.5$, $\epsilon_1' = 6.25$, $\epsilon_1'' = 1.65$, and $\epsilon_2 = 2.25$,[10] we estimate the filling factor to be $p \simeq 3 \times 10^{-3}$. As can be seen from Eq. (1), changes of the absorption coefficient of the semiconductor by a small amount $\Delta\alpha_1$ change the absorption coefficient of the composite material changes accordingly: $\Delta\alpha_c/\alpha_c = \Delta\alpha_1/\alpha_1$.

A colliding pulse mode-locking (CPM) laser provides optical pulses with a duration of 60 fs and 100 MHz repetition rate at $\lambda = 620$ nm. The output of the CPM laser is divided into probing and exciting pulses. The exciting pulse train is chopped and focused onto the sample. The energy density of the excitation pulses was $W_0 = 10^{-5}$ J/cm^2. The exciting femtosecond pulse generates an electron-hole plasma with a carrier density $N = W_0\alpha_c/ph\omega = 3 \times 10^{17}$ cm^{-3} for $\alpha_c \simeq 30$ cm^{-1} in the semiconductor inclusions. The probing pulses are delayed by an optical delay line and travel noncollinearly through the sample. Probing and exciting pulses are polarized perpendicularly to each other. Light induced changes of the absorption are measured by a phase sensitive detection system. The filter glasses (50 mm diameter, absorbance $A \simeq 0.5$) were glued onto fused-silica substrates and rotated at 1300 rpm to avoid sample heating. Time zero was determined by replacing the sample by a 150-μm-thick potassium dihydrogen phosphate (KDP) crystal and measuring the cross-correlation trace. All samples were studied at room temperature.

Figure 2 shows the time-resolved absorption changes for the samples 1 to 3 of Fig. 1. The change of absorbance $\Delta A = 0.43\,\Delta\alpha \times 1$ is plotted versus delay time between exciting and probing pulse for the time interval of the first 500 fs. The dashed curves are the cross-correlation traces determining time zero. In the insert of Fig. 2 the relevant optical transitions are indicated schematically. For sample 1 [Fig. 2(a)], the trace exhibits an initial fast decrease of the absorbance corresponding to the generation of electrons and holes, thereby reducing the number of optically connected states. The absorbed photons supply a large excess energy $\Delta E = h\omega - E_g \simeq 550$ meV to the carriers in this sample, thus leading to a very hot distribution of the carriers. The high-energy tail of this hot distribution is responsible for the absorbance decrease at early times, i.e., for $t_D \leqslant 100$ fs. For $t_D > 100$ fs, rapid absorption recovery with a time constant of 200 ± 20 fs is observed. This process can be identified with the cooling of the hot-carrier distribution down to the lattice temperature T_L. A comparison with the expected energy loss rate of the electron gas due to emission of longitudinal optical (LO) phonons in the corresponding bulk semiconductors[11] yields relaxation times of about 300 fs, being slightly larger than the observed 200 fs. For sample 3 [Fig. 2(c)] the excitation energy is only slightly larger than E_G, resulting in an excess energy of $\Delta E = 30$ meV. Here, the absorbance decrease ΔA integrates over the duration of the excitation pulse and remains essentially constant for the
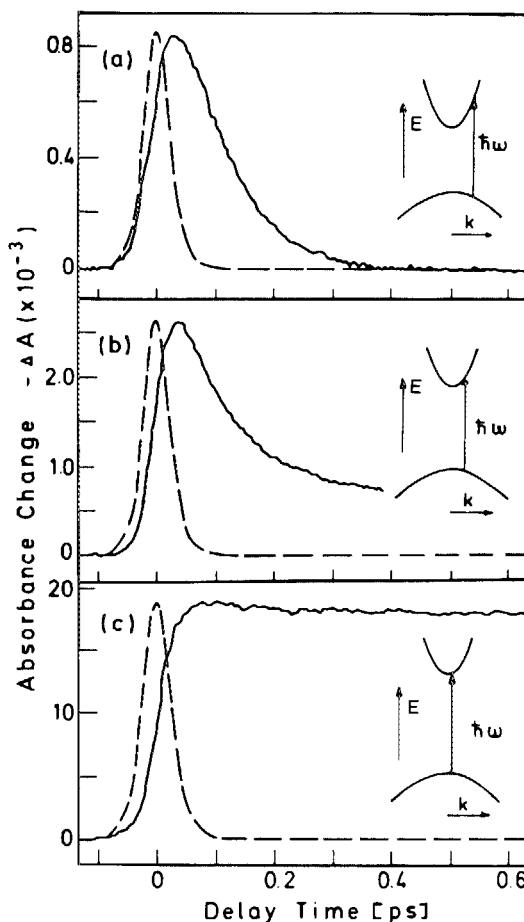

FIG. 2. Absorbance changes (solid curves) induced by a femtosecond light pulse ($\lambda = 620$ nm, $t_p = 60$ fs) as a function of delay time. The dashed traces indicate the cross correlation of exciting and probing pulses. The time evolution of the absorbance changes strongly depends on the excess energy ΔE [550 meV, 300 meV, and 30 meV for samples 1 to 3 of Fig. 2(a)–(c), respectively]. The insert schematically shows the respective optical transition.

plotted time range. No subpicosecond process is observed. Obviously, due to the low carrier excess energy, the distribution function at a time of 100 fs is close to the distribution function at later times. The trace can be described by filling of the conduction-band states with a thermalized carrier distribution at $T = T_L$. Eventually, electron-hole recombination restores the original absorbance with a time constant of 100 ± 25 ps (not shown in the figure). This relatively short recombination time is not unreasonable in light of the large number of interface states due to "dangling bonds" at the surface of the semiconductor microcrystallites. We also observe smaller components of ΔA, decaying with time constants of several nanoseconds, as can be expected from recombination at different recombination states. Sample 2 [Fig. 2(b)] represents an intermediate case with an excess energy $\Delta E_c = 300$ meV. Here, a fast component (time constant 250 ± 40 fs) is followed by a slower relaxation process with a time constant of 80 ± 10 ps (not shown in the figure). In accordance with the preceding cases, for early times $t_D < 500$ fs, cooling of the electron distribution reduces the ΔA values quickly, while electron-hole recombination gives rise to the much slower relaxation process with the time constant of 80 ps.
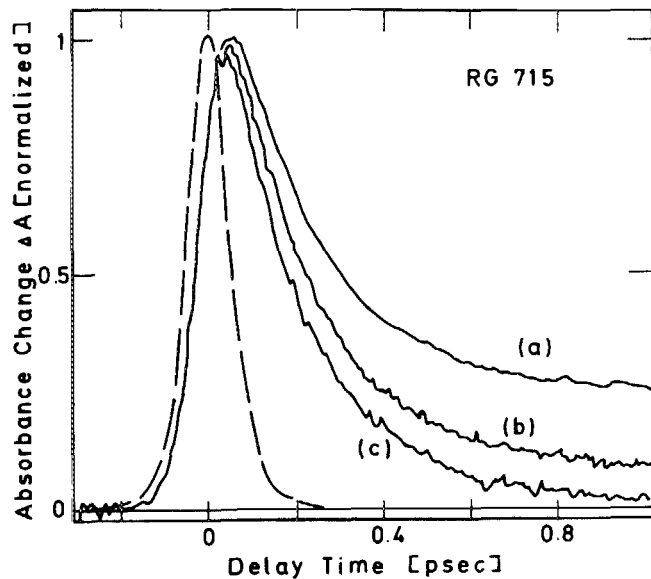
FIG. 3. Absorption recovery of the semiconductor-doped glass sample 2 for different excitation energies E_0, $E_0/2$, and $E_0/4$ (from top to bottom). The curves are normalized to the same excitation energy. A nonlinear decrease of ΔA for times ~500 fs with excitation energy and hence carrier density is observed.

Additional valuable information can be obtained from this semiconductor glass (sample 2) by variation of the optical excitation energy. Figure 3 plots three absorption recovery traces for different excitation energies and hence different injected carrier densities. The upper trace is identical to Fig. 2(b) ($N = 3 \times 10^{17}$ cm^{-3}); the lower traces correspond to 2 and 4 times attenuated laser pulses, respectively. The traces were normalized to the incident pulse energy. A significant nonlinear decrease of ΔA with carrier density for times ⩾500 fs is observed, whereas the peak absorption decrease (at t_D ~60 fs) scales linearly with the injected carrier density.

These data can be explained by a carrier density dependent band filling process. In particular, the best candidate for such a process is trapping into shallow traps, acting as a sink for the conduction-band electrons. If the density of these levels is about the same as the injected carrier density and the trapping time of the same order of magnitude as the LO-phonon relaxation, the transition into the trap levels becomes saturated. Hence, a superlinear dependence of ΔA on carrier density is observed in Fig. 3. Consequently, the 200–

250 fs relaxation process observed in the semiconductor-doped glasses RG 830 and RG 715 is a combination of cooling of the electron gas due to LO-phonon emission and trapping into shallow traps. Subsequently, electron-hole recombination at surface states close to the middle of the band gap takes place with a time constant of 85–100 ps. We would like to emphasize that in the semiconductor glass RG 645 (sample 3), we could not observe a nonlinear dependence of ΔA on carrier density. This observation confirms our hypothesis of shallow traps only a few tens of meV below the band gap being responsible for the carrier density dependent band filling process. The broad bandwidth of the femtosecond optical pulse (~20 meV) covers in this filter the semiconductor band edge as well as the energy levels of the shallow traps and is therefore insensitive to the relaxation process from the conduction band to the shallow traps.

In conclusion, we have found very fast absorption recovery in semiconductor-doped glasses after carrier generation with a femtosecond optical pulse of 60 fs duration. The same relaxation processes of photoexcited carriers as in crystalline semiconductors, i.e., cooling of the hot-electron distribution by LO-phonon emission and bandfilling, are also observed in semiconductor-doped glasses. But unlike in bulk semiconductors, we find subpicosecond carrier trapping into shallow traps at least partly responsible for the measured 200 fs relaxation times. Electron-hole recombination time is found to be decreased to ~100 ps due to the large number of surface states in the semiconductor microcrystallites.

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