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OPTICAL PROPERTIES OF MULTILAYER HETEROSTRUCTURES BASED ON ZINC CHALCOGENIDES UPON STRONG LASER EXCITATION

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We have carried out an experimental study of the nonlinear optical properties of multilayer heterostructures based on zinc chalcogenides when excited by ultrashort laser pulses. We have observed a strong change in the optical properties of the samples over a broad spectral region for two-photon and one-photon excitation of the ZnSe sublattice. The fast relaxation time of the nonlinearity is ~2–5 psec in both cases. We propose a physical model qualitatively explaining the observed effects.

Key words: *multilayer heterostructures, ultrafast processes, electron-hole plasma.*

Introduction. Study of heterostructures is important not only because of their practical value for designing optical devices but also because of the importance of studying fundamental physical processes occurring in semiconductor compounds on interaction with laser radiation. Multilayer heterostructures provide a basis for designing nonlinear optical components: modulators, switches, chirp mirrors. In such devices, the intrinsic nonlinearity of semiconductor materials can be enhanced as a result of phenomena connected with spatial confinement of electromagnetic wave propagation, such as formation of a photonic bandgap in a multilayer periodic structure (photonic crystal); localization effects in single and coupled microcavities; polariton effects in coupled quantum wells [1–4].

Zinc selenide is a well studied and actively used material. This is a major component for designing semiconductor lasers and light-emitting diodes emitting in the blue region of the spectrum. It also has strong nonlinear optical properties; in particular, coherent phenomena of different orders, exciton and polariton nonlinearity [5, 6], and optical bistability [7] are observed in it.

With strong laser excitation, a dense nonequilibrium electron-hole (e-h) plasma is formed in semiconductor materials. The major contribution to plasma relaxation processes comes from scattering off charge carriers and polar optical phonons and also intervalley scattering, characterized by fast temporal response. For high concentrations of free carriers ($\approx 10^{-19}$–10^{-20} cm^{-3}), the plasma frequency is shifted to the visible region of the spectrum, which leads to a change in the optical properties of the semiconductor in the transparency region. In multilayer heterostructures, selective excitation of one of the components is accompanied by a change in the optical properties of the entire structure as a whole.

The combination of strong intrinsic nonlinearity of zinc selenide with the presence of a photonic bandgap makes multilayer heterostructures based on it unique objects of study.

In this paper, we present the results of a study of the nonlinear optical properties of multilayer heterostructures based on zinc chalcogenides for different excitation conditions.

Experimental Section. Multilayer ZnSe/ZnS heterostructures were obtained by chemical vapor deposition from heteroorganic compounds [8]. They were grown in the system $Zn(C_2H_5)_2$–$(CH_3)_2Se$–$(C_2H_5)_2S$ with a hydrogen pressure close to atmospheric, in a quartz slot reactor at temperatures of 425°C–470°C, on (100) substrates of single-crystal gallium arsenide wafers. Before growth was started, the substrate was held for 5 min at 600°C in a stream of

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hydrogen in order to remove the oxide layer. In order to eliminate the appearance of defects due to the difference in lattice constants for GaAs and ZnS, the heterostructure was grown on a buffer layer of ZnSe. Growth of single crystal layers of ZnSe and ZnS were ensured with flowrates of $Zn(C_2H_5)_2$, $(CH_3)_2Se$, and $(C_2H_5)_2S$ of respectively 5.5, 10.4, and 11.8 μmol/min in the selected temperature range. In order to achieve a mirror-smooth surface, diethylzinc was fed to the reactor 1–2 sec before growing each subsequent layer. In growing the heterostructures, the thicknesses of the individual layers were set by the growth rates. The quality of the heterostructures was assessed by photoluminescence and x-ray diffractometry methods, and the thicknesses were determined by ellipsometry and reflection spectra.

The thicknesses of the layers were selected so that the maximum reflection of the Bragg mirror was located close to the fundamental absorption edge of ZnSe.

The nonlinear optical properties were studied using a femtosecond spectrometer [9] based on an original femtosecond titanium:sapphire pulse generator [10], simultaneously pumped by a pulsed Nd:YAG laser with passive mode locking and negative feedback and also by a regenerative amplifier. This system makes it possible to obtain pulses of duration τ = 150 fsec and energies up to 1 mJ with frequency 10 Hz, tunable in the spectral range 760–820 nm. Pulses of the fundamental frequency, obtained at the amplifier output, are split into two parts in 1:4 ratio. The more intense beam (or its harmonic), after passing through a controllable delay line, is used as the pump pulse. A change in the pump radiation power density in the sample probing region was achieved by longitudinal displacement of the focusing lens. The induced nonlinearity was probed using the supercontinuum generated when focusing the smaller fraction of the pulse of the fundamental frequency on a cuvet containing water with path length 1 cm. The continuum emission was split by a semitransparent mirror into two pulses of identical intensity (the reference pulse and the signal pulse), which were focused on the sample using mirror optics. The reference pulse is incident on the test sample before the arrival of the excitation pulse, while the signal pulse is incident with a delay relative to the excitation pulse. The spectra of both pulses for each laser flash were recorded and processed by a system based on a polychromator, a CCD array, and a microprocessor.

We used the first and second harmonic of the emission from a titanium-doped sapphire laser with wavelengths 780 nm and 390 nm, pulse energies 250 and 20 μJ respectively.

The experimental dependences have a complicated shape and can be approximated by a two-exponential function

$$\Phi = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (1)$$

where τ_1 and τ_2 are time constants; A_1, A_2 are weighting factors describing the rise and decay of the nonlinear process. The resulting curves are the convolution of this function with the instrumental function of the spectrograph. The accuracy of the approximation was estimated from the least sum of the squares using the Levenberg–Marquardt method.

Results and Discussion. The studied structures are alternating thin layers (~50–60 nm) of semiconductor materials with different refractive indices, forming a Bragg mirror. By selectively exciting the ZnSe sublattice in such a structure, we vary its refractive index and consequently the optical properties of the entire structure.

In the region of the spectrum where both components of the material do not absorb, all the samples have a reflection spectrum typical of periodic dielectric mirrors. We studied the optical properties of heterostructures with different numbers of periods. In all the experiments, we observed a shift of the Bragg reflection bands and fast relaxation of the nonlinear response on the order of a few picoseconds over the entire recorded spectral range (450–1100 nm).

We have studied the nonlinear optical properties of heterostructures containing 15 pairs of ZnSe/ZnS layers. The results are presented as differential reflection and transmission spectra and the kinetic curves for relaxation of the nonlinear response.

Figure 1 shows the linear and differential reflection spectra of a multilayer heterostructure on a GaAs substrate for one-photon and two-photon excitation. The shape of the differential reflection spectra allows us to conclude that on excitation of the samples, the reflection bands are shifted toward shorter wavelengths, due to a change in the refractive index of the zinc selenide.

The reflection spectra of the studied multilayer structures were numerically modeled using the transfer matrix method. Comparing the calculated and experimental spectra shows that the observed shift in the reflection spectrum is caused by a change in the refractive index of zinc selenide by about –0.05.

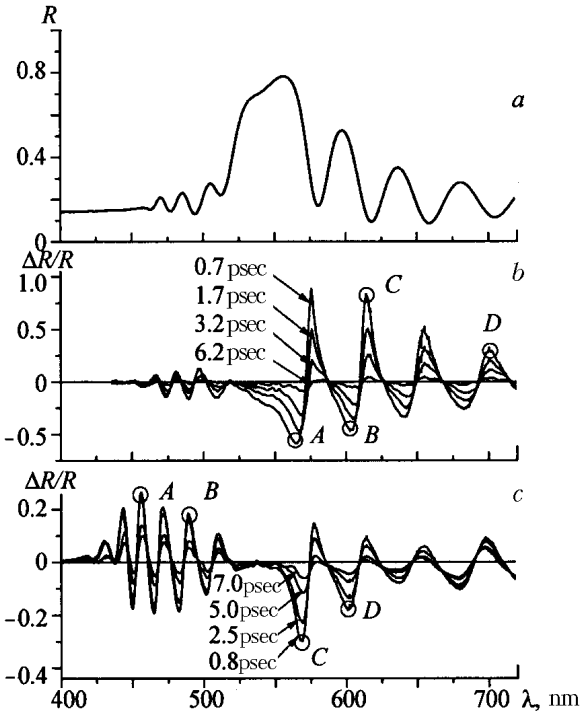

Fig. 1 Reflection spectra (a) and differential spectra for the multilayer heterostructure GaAs/$ZnSe_{105\ nm}(ZnS_{55\ nm}ZnSe_{53\ nm})_{15}$ on excitation by pulses of duration 150 fsec, λ_{ex} = 390 nm (b) and 780 nm (c); points labeled by letters correspond to the relaxation curves on Fig. 2.

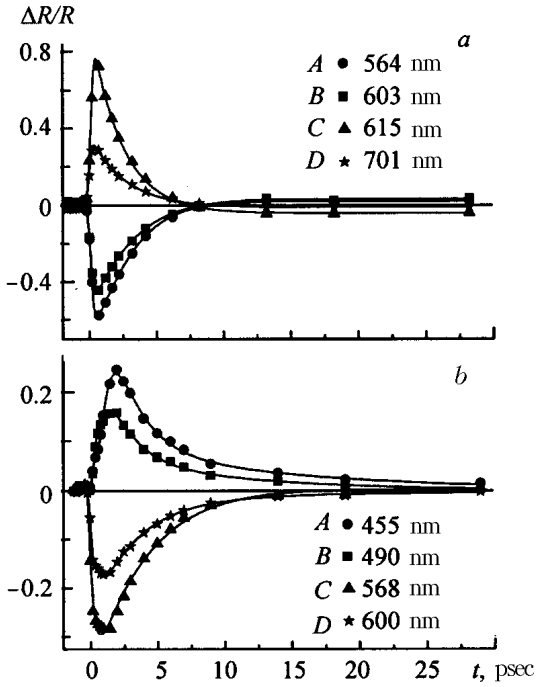

Fig. 2 Relaxation kinetics of induced changes in the reflection of a multilayer heterostructure with laser excitation by pulses of duration 150 fsec, λ_{ex} = 390 (a) and 780 nm (b).

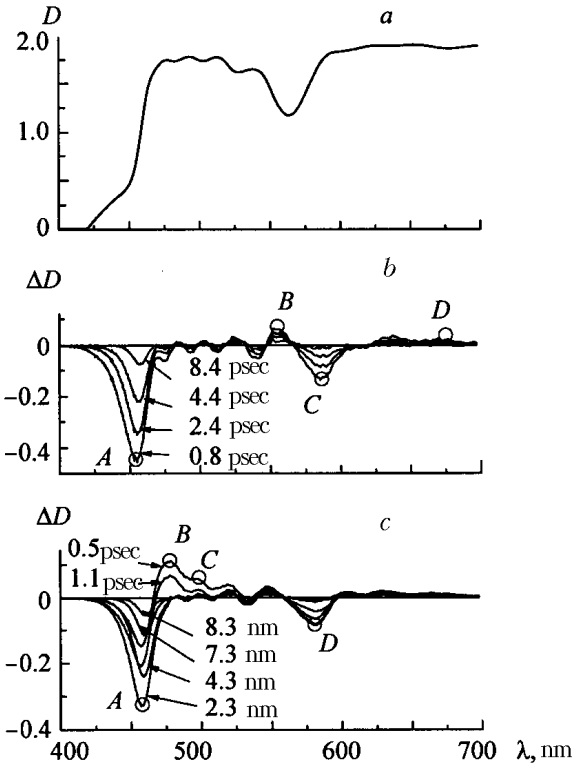

Fig. 3 Optical density spectra (a) and differential absorption spectra of a multilayer heterostructure with removed GaAs substrate on excitation by pulses of duration 150 fsec, λ_{ex} = 390 nm (b) and 780 nm (c); points labeled by letters correspond to the relaxation curves on Fig. 4.

The kinetics of the induced changes in the reflection are shown in Fig. 2. In the case of one-photon pumping, we observe a monoexponential dependence with relaxation time constant ~2 psec and rise kinetics coinciding with the instrumental function of the spectrometer. For two-photon excitation, an additional rise is detected in the kinetics, with $\tau \sim 300$ fsec.

The structures with removed GaAs substrate allow us to eliminate any possible effect from the substrate in the nonlinear response in the heterostructure (for example, carrier diffusion or energy transport to the substrate). At the same time, the opportunity arises to study not only reflection from a periodic structure but also the transmission spectra, containing information about nonlinear absorption. The spectra of the variation in the optical density for the samples with removed substrate are shown in Fig. 3. In the spectrum, in addition to changes connected with the shift of the Bragg mirror bands with characteristic times corresponding to those presented above, there is a strong band in the 450 nm region due to the change in the absorption spectrum near the edge of the bandgap for ZnSe. We should note that the relaxation time for this band is longer than the relaxation time for the other regions of the spectrum (Fig. 4a).

For two-photon excitation of multilayer heterostructures with removed GaAs substrate, the relaxation kinetics take on a more complicated shape (Fig. 4b). Both for one-photon and for two-photon excitation, the relaxation time in the spectral region corresponding to the ZnSe absorption edge is appreciably longer than the times for the remaining regions of the spectrum. Furthermore, in this spectral region there is a considerable delay in the rise of induced absorption. For the 470–520 nm region of the spectrum, we observe rapid darkening (~1 psec), which then is suppressed by bleaching.

The observed ultrafast changes occurring over a broad spectral range can be explained by processes involving appearance and relaxation of an e-h plasma in zinc selenide. Strong laser excitation leads to the appearance of a hot plasma, where the average kinetic energy of an e-h pair is ≈0.3 eV, with carrier temperature ≈3500 K.

The contribution of the plasma to the dielectric constant is described by the formula [11]

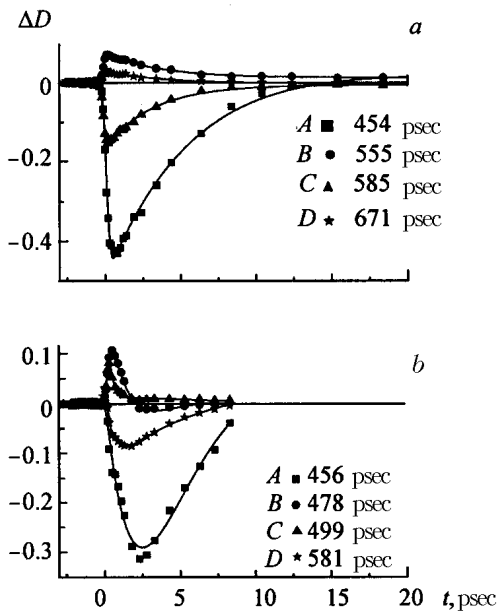

Fig. 4 Relaxation kinetics of induced optical density of a multilayer heterostructure with removed GaAs substrate on laser excitation by pulses of duration 150 fsec, λ_{ex} = 390 nm (a) and 780 nm (b).

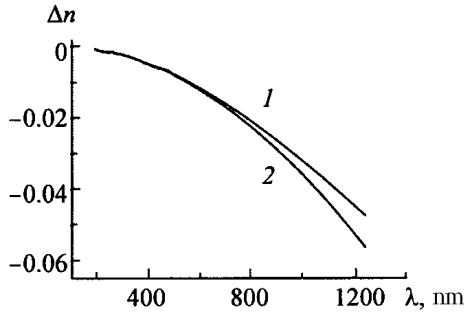

Fig. 5 Change in the refractive index for carrier concentration $N = 10^{19}$ cm^{-3} and relaxation time 10^{-14} sec (1) and 10^{-12} sec (2).

$$\varepsilon = \varepsilon(0) + i\varepsilon'(0) - \frac{Nq^2}{\mu\left(\omega^2 + \frac{i\omega}{\tau}\right)} \equiv (n + ik)^2, \qquad (2)$$

where $\varepsilon(0) + i\varepsilon'(0)$ is the dielectric constant in the absence of excitation; N is the carrier concentration; $q^2 = e^2/4\pi\varepsilon_0$; μ is the effective mass; ω is the frequency; τ is the relaxation time.

This relation gives the values of the imaginary and real parts of the dielectric constant as a function of the concentration and cooling time for the e-h plasma. Figure 5 shows the curves for the change in the refractive index for a carrier concentration $N = 10^{19}$ cm^{-3} and different relaxation times. The change in the absorption coefficient can be neglected because of its insignificant value.

After thermalization (≈100 fsec), the plasma begins to cool down, where the temperature of the lattice and the e-h plasma equalize, i.e., the excess energy of the e-h plasma above E_g is consumed in generation of optical polar

phonons. The two systems (e–h and phonon) give opposite signs for the change in the refractive index, and so the contribution of the e-h plasma to the refractive index is compensated by the contribution of phonons with delay corresponding to the time for cooling the plasma down to E_g, the phonon generation time (≈1 psec). This process is dominant in the transparency region of the materials.

Near the edge of the bandgap, the picture is considerably more complicated. An additional contribution to the change in the optical properties comes from the decrease in the bandgap width and also filling of the bottom of the conduction band and the top of the valence band by carriers as they cool down.

In the case of two-photon pumping, the induced changes in the optical properties in the heterostructures are determined by the same processes. However, we must note some characteristic features of two-photon excitation which may be the reason for the typical differences observed in the differential spectra in this case: the need for a significant increase in the excitation intensity compared with the one-photon pumping case, due to the small value of the two-photon absorption coefficient, which leads to the appearance of fast coherent effects, and also more uniform pumping of the entire volume of the studied structure.

Conclusion. The results obtained from studies of multilayer heterostructures based on ZnSe/ZnS demonstrate that strong laser excitation of the ZnSe sublattice by ultrashort pulses leads to significant changes in the reflection and transmission over a broad spectral range for the entire structure. The strong nonlinear response to 2–5 psec duration is connected with the process of the electron-hole plasma cooling down, accompanied by generation of optical phonons.

The presence of such significant and fast changes in the optical properties of multilayer heterostructures allows us to use them as a basis for complete realization of optical ultrafast devices for fiber-optic communication lines. An important feature of such devices is the possibility of controlling the optical properties in the required spectral range by varying the parameters of the structure itself.

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