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Energy transfer processes via the interface of ZnSe/GaAs epilayers

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Abstract

In the present paper, energy transfer processes via the interface of molecular beam epitaxy (MBE) grown ZnSe/GaAs epilayers are investigated by means of time-resolved photoluminescence spectroscopy. High excitation experiments show that an electron–hole plasma exists in free-standing ZnSe layers only. By comparing the time-resolved luminescence properties of ZnSe/GaAs heterostructures and of free-standing ZnSe layers, we demonstrate which kind of energy transfer mechanism is predominant in heterostructures: At low excitation densities energy is transfered by re-absorption of the ZnSe luminescence. At higher excitation densities, an ambipolar carrier diffusion via the ZnSe/GaAs interface is the dominating process.

1. Introduction

In the past decade, ZnSe epilayers have been the object of intense research in view of possible application to optoelectronics. The improvement in growing pure crystalline ZnSe by epitaxial growth methods, especially by molecular beam epitaxy (MBE), recently culminated in the first registered blue laser activity in a ZnSe-based device [1]. However, the responsible process for this lasing is still not well understood. Therefore, it is necessary to study the nonlinear optical processes in such epilayers, and especially, to understand the influence of the substrate on these nonlinearities.

Time-integrated photoluminescence of ZnSe/GaAs heterostructures under low CW excitation densities ($I_{exc} < 5$ mW/cm^2) has been thoroughly investigated [2,3]. In the excitonic regime the luminescence depicts split exciton recombination lines, X_{lh} and X_{hh}, and split bound exciton emission lines, I_2 and I_2'. This splitting of the excitonic features is correlated with the splitting of the upper Γ_8 valence band of ZnSe, because of the strain induced by the lattice mismatch (0.27% at room temperature) and the different thermal expansion coefficients of layer and substrate [2]. Time-resolved luminescence of free excitons in the investigated heterostructures yields decay times of 100 ps for the X_{hh} exciton and 150 ps for the X_{lh} exciton [3]. The photoluminescence of the ZnSe/GaAs heterostructures under high-density excitation of a ns pulse laser shows two strong bands, which are called P_2 and P_∞. They have been assigned to exciton–exciton collision processes [4,5]. In contrast to the heterostructures, the photoluminescence of highly excited free-standing ZnSe layers (obtained after a specially developed etching procedure of the GaAs sub-

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strate) depicts an additional N band on the low energy side of the P bands, which has been interpreted as the recombination of electron–hole pairs in an electron–hole plasma (EHP) [6]. This means the carrier density seems to be higher in layers without substrate and points out that energy transfer processes are present in the ZnSe/GaAs heterostructures.

In this paper we investigate the kind of energy transfer processes from the ZnSe layer into the GaAs substrate in ZnSe/GaAs heterostructures. We first compare the luminescence dynamics of ZnSe/GaAs heterostructures to those of free-standing ZnSe layers under low and high excitation densities with ps time-resolution. Afterwards, we investigate the dynamics of the GaAs substrate luminescence upon excitation of the ZnSe epilayer to distinguish between the different possible energy transfer mechanisms via the interface of the ZnSe/GaAs heterostructure.

2. Experimental setup

All ZnSe samples were nominally undoped single-crystal MBE layers with thicknesses of 1 to 2 μm. The growth conditions on (100) undoped GaAs substrates have been described in an earlier publication [7]. In order to have free-standing ZnSe layers, we used a chemical etching procedure of the GaAs substrate, described in ref. [4]. The samples were immersed in liquid He at 1.8 K. In time-resolved luminescence experiments, a dye-laser synchronously pumped by an activeley mode-locked frequency-tripled Nd:YAG laser with 3 ps pulse duration and 3.8 MHz repetition rate excited the samples. The luminescence transients were detected through a time-compensated double monochromator by means of time-correlated single photon counting using a multi-channel-plate photomultiplier. The ps laser system yields excitation densities up to 350 MW/cm^2 in the used configuration. The luminescence transients were fitted by convolution of the apparatus response to the exciting 3 ps laser pulse with a sum of two exponential functions. This sum describes the investigated transition and has the rise time τ_{rise} and the decay time τ_{decay} of the transition as fitting parameters. This convolution technique allows a time resolution better than 10 ps.

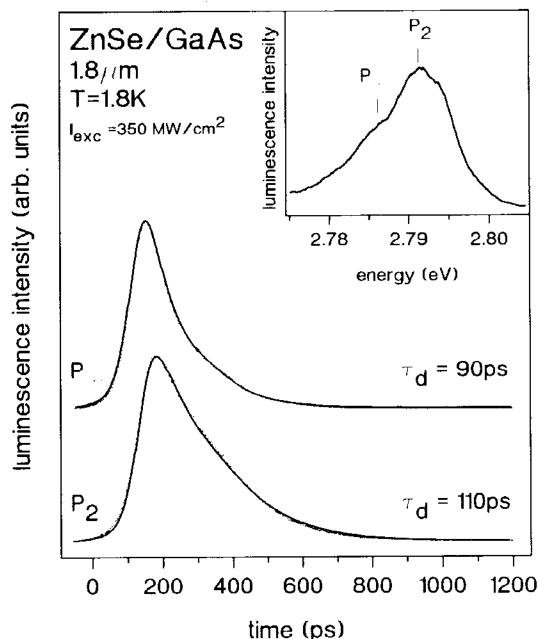

Fig. 1. Luminescence transients of the P_2 and P_∞ bands in the emisision of ZnSe/GaAs heterostructures in the excitonic regime under high band-to-band excitation densities (E_{exc} = 2.83 eV and I_{exc} = 350 MW/cm^2) with a ps laser system described in the text. The insert shows the corresponding time-integrated luminescence for the same experimental conditions.

3. Time-resolved results

3.1. ZnSe / GaAs heterostructures

For a laser energy above the ZnSe band gap and at high ps excitation densities (> 300 MW/cm^2), the time-integrated luminescence of ZnSe/GaAs heterostructures shows two strong bands on the low energy side of the excitonic regime which are called P_2 and P_∞ (see insert of Fig. 1). They have been attributed to exciton–exciton collision processes, where one exciton is scattered in an upper excitonic polariton branch ($n = 2, \ldots, \infty$), while the other exciton is scattered in the lower photonic branch under energy and momentum conservation and is then detected as

a photon leaving the crystal [8]. Considering the conservation laws, the photon detected at the energy position of the P_2 band stems from an exciton, which originates from the neighbourhood of the bottleneck, because its collision partner has been scattered in the $n = 2$ polariton branch. In the case of the photon detected at the energy position of P_∞, it has a lower energy than the photon of the P_2 band, and therefore originates from an exciton which is more distant from the bottleneck. It is already known that polaritons which are in the vicinity of the bottleneck of the polariton dispersion curve have a relatively longer life time [9]. The decay time of the P_2 band (= 110 ps) is found to be greater than that of the P_∞ band (= 90 ps) (Fig. 1). This underlines the correlation of the polariton dispersion with the decay times of the P bands, and supports the interpretation of these bands in terms of excitonic collision processes.

3.2. Free-standing ZnSe epilayers

By removing the GaAs substrate, a relaxation of the strain in the free-standing ZnSe layer is observed. Therefore, the luminescence and absorption spectra of such layers depict only one degenerate free exciton and one bound exciton feature. Time-resolved measurements show that the lifetime of the free exciton in those free-standing ZnSe layers (= 200 ps) is much longer than that in a ZnSe/GaAs heterostructure. This means that the strain in the heterostructure together with the interface defects and dislocations actually reduce the lifetime of free excitons.

The luminescence transient of the P_2 band depicted in Fig. 2 has a decay of 170 ps. The decay of the P_∞ band has been measured at the same sample and amounts to 110 ps: In both cases, we see that the luminescence of the P bands behaves similarly to the free exciton luminescence having longer decay times in free-standing ZnSe layers than those in ZnSe/GaAs heterostructures. This is again consistent with the interpretation of the high-density P bands as exciton–exciton collision processes.

The time integrated luminescence spectrum of free-standing ZnSe layers shows an additional N

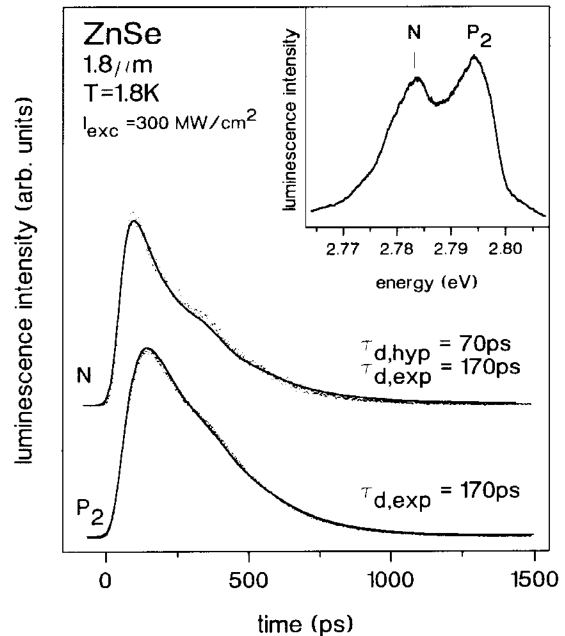

Fig. 2. Luminescence transients of the N and P_2 band in the emission of highly excited free-standing ZnSe layers for the same laser energy as in Fig. 1 and with $I_{exc} = 350$ MW/cm^2. The insert depicts the corresponding time integrated luminescence.

band for excitation densities above 300 MW/cm^2 (see insert in Fig. 2), which has been interpreted in terms of electron–hole plasma recombination [6]. As the N band superimposes the P_2 band, the theoretical fit of the N transient contains an exponential part of about 50% decaying with the corresponding $\tau_{d,exp} = 170$ ps. The remaining experimental transient of the N luminescence band (Fig. 2) can only be fitted by a hyperbolic decay function ($\tau_{d,hyp} = 70$ ps) with deconvolution of the luminescence transient, which actually corresponds to an EHP luminescence decay process [10]. At even higher excitation densities we register that the transient of the N band shows a very fast decay time of about 10 ps, which indicates the beginning of stimulated emission processes.

3.3. Energy transfer processes in ZnSe / GaAs epilayers

The fact that an EHP can be built up only in a free-standing ZnSe layer and not in a ZnSe/GaAs

heterostructure demonstrates that the carrier density is limited in a ZnSe/GaAs heterostructure. To show that ambipolar carrier diffusion actually takes place via the interface, we use the GaAs luminescence as a detector to investigate the excitation mechanism. When a band-to-band excitation of the ZnSe layer of a ZnSe/GaAs heterostructure is applied, we observe the luminescence of both ZnSe and GaAs, which means that an excitation of the GaAs substrate is present. For the used excitation energy, the laser light is strongly absorbed in the first 0.1 μm of the ZnSe layer ($\alpha \approx 10^5$ cm^{-1} [11]), and cannot be the source of the excitation in the GaAs substrate.

Actually we have to consider two main types of excitation mechanisms in order to explain the observed excitation of the GaAs substrate (see Fig. 3):

(1) Excitation by light transfer: the emitted ZnSe luminescence light is absorbed in the GaAs substrate and creates electron–hole pairs, which then recombine. In this case the GaAs luminescence transient has to be fitted by convolution of the corresponding ZnSe luminescence transient with a two-exponential function (describing the investigated transition in GaAs).

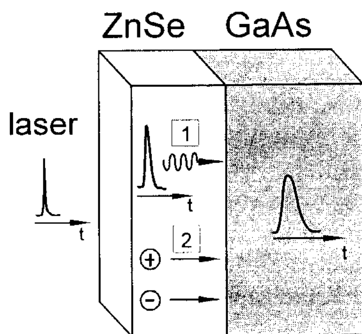

Fig. 3. Schematical presentation of the different kinds of excitation of the GaAs substrate. The laser excites the ZnSe layer with an energy greater than the band gap and is completely absorbed. In process (1), the ZnSe layer emits blue light with its proper dynamics, which transfers into the GaAs substrate, where it causes an excitation of the substrate. In process (2), the photogenerated carriers at the surface of the ZnSe layer diffuse into the GaAs substrate and cause there an excitation. The time-resolved GaAs luminescence allow us to determine which excitation process is predominant.

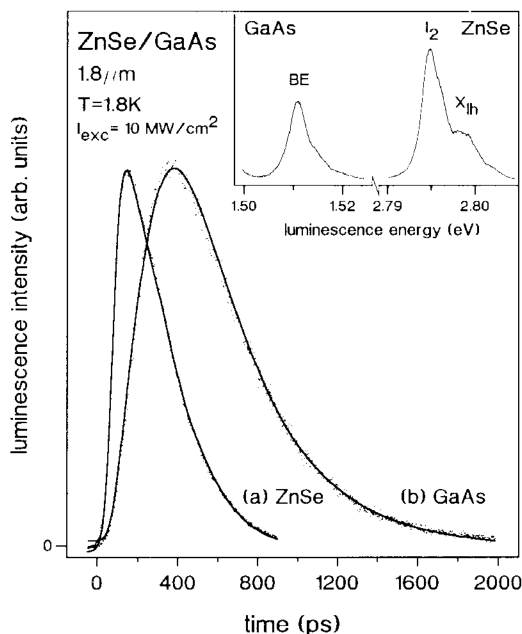

Fig. 4. Luminescence transients of the blue emission of the ZnSe layer and the red emission of the GaAs substrate in the excitonic regime under band-to-band excitation with $I_{exc} = 10$ MW/cm^2. The insert shows both types of time-integrated luminescence detected simultaneously. The full curves are the fits obtained from convolution techniques described in the text.

(2) Excitation by free carriers, which diffuse ambipolarly from the ZnSe layer into the GaAs substrate: this process is favoured by the specific band offset structure of the heterostructure of type I [12]. There, we expect that this type of excitation starts delayed at a time given by the ambipolar diffusion of the photogenerated carriers through the 1–2 μm ZnSe layers. In this case the GaAs transient has to be fitted by convolution of the sum of two exponential functions with given rise and decay times with the apparatus response and taking into account the occurring delay time.

The insert of Fig. 4 shows the time integrated luminescence spectra in the excitonic ranges of the ZnSe layer and of the GaAs substrate under low excitation densities of the layer ($E_{exc} = 2.83$ eV and $I_{exc} = 10$ MW/cm^2). The simultaneous detection of both types of luminescence is possible under the same experimental conditions, be-

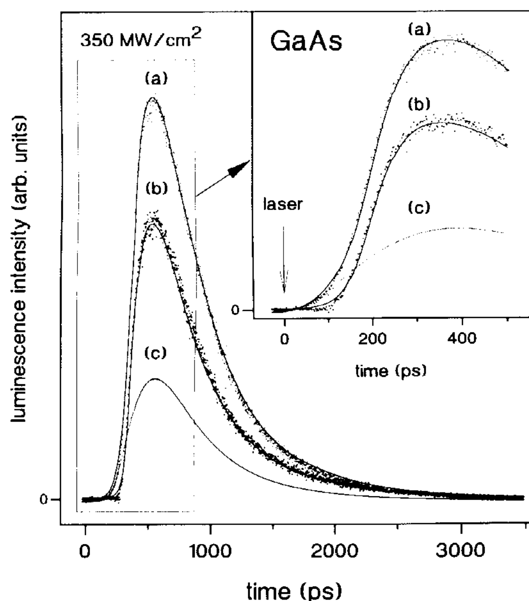

Fig. 5. (a) Luminescence transient of the emission of the GaAs substrate detected by band-to-band excitation of the ZnSe layer in a heterostructure at high excitation densities ($I_{exc} = 350$ MW/cm^2). (c) calculated GaAs luminescence transient if light transfer is assumed as the excitation process and amounts to 30%. (b) calculated transient if the excitation takes place through carrier diffusion and amounts to 70%.

cause the red luminescence of the GaAs substrate passes undisturbed through the ZnSe layer. Fig. 4 depicts the corresponding transients of the bound exciton luminescence maxima of ZnSe (a) and of GaAs (b). The predominant luminescence of ZnSe (I_2) decays within 150 ps. The bound-exciton luminescence transient of GaAs can be fitted very good by convolution of the recorded I_2 transient (and not the apparatus response of the laser pulse) with a two-exponential funtion ($\tau_{rise} < 90$ ps and $\tau_{decay} = 350$ ps). This indicates that here the light transfer is the only responsible excitation mechanism of the GaAs substrate.

For excitation densities above 300 MW/cm^2, the excitation mechanism of the GaAs obviously changes: The recorded transients of the GaAs luminescence cannot be fitted if we assume only light transfer between layer and substrate. In Fig. 5 we show the transient of the GaAs luminescence in the excitonic range at its energetic maximum (a). In order to fit properly the GaAs transient we have to consider two components:

The first one is depicted by curve (c) and represents the part of the light transfer (about 30%), which is obtained by convolution of the corresponding ZnSe luminescence transient with a two-exponential function ($\tau_{rise} < 80$ ps and $\tau_{decay} = 560$ ps).

The second part is depicted by curve (b) and represents the part of the carrier diffusion (about 70%). This part results from convolution of the apparatus response to a delta-like excitation (e.g. the 3 ps laser pulse) with a two-exponential funtion with the same rise and decay times ($\tau_{rise} < 80$ ps and $\tau_{decay} = 560$ ps). However, we have to consider an additional delay time of about 160 ps for the fit (b) in order to reach a fit of the GaAs luminescence transient (a), as the sum of curve(b) and curve (c). This delay time can be understood as the time needed for the carriers to reach the substrate. With a thickness of about 2 μm and a registered delay time of 160 ps, we obtain a diffusion velocity of 1.2×10^6 cm s^{-1} corresponding to results obtained in CdS bulk crystals [13]. With these results, we prove that at high excitation densities, the ambipolar carrier diffusion via the interface plays an increasing role, in addition to the light transfer.

In this paper, we demonstrate that above a certain high excitation density (> 300 MW/cm^2), carrier diffusion via the interface of ZnSe/GaAs heterostructure becomes important, which represents an energy loss in the ZnSe layer. In this context, it explains why an EHP cannot be built up in those heterostructures. However, if we consider that the decay time of the EHP (= 100 ps) is shorter than the diffusion time of the carriers through the ZnSe layer (= 160 ps), it should be possible to see plasma luminescence also in the ZnSe/GaAs heterostructure. As this is not the case, we take into account additional mechanisms which prevent the carrier density from increasing. As greater decay times of the P bands are measured in the free-standing ZnSe layer, this shows that the strain situation in ZnSe/GaAs heterostructure actually reduces the decay times, which represents also a competing process reducing the carrier density.

4. References

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