

DEGENERATE-FOUR-WAVE-MIXING AT THE NITROGEN ACCEPTOR BOUND EXCITON IN ZnSe EPILAYERS

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This contribution reports on the energy relaxation and the dephasing of the (A^0_N, X)-complex in ZnSe. The results obtained from time-resolved luminescence and degenerate-four-wave-mixing experiments with pico- and femtosecond excitation are presented and discussed in view of impurity interactions and scattering of free excitons. From nonlinear quantum beat spectroscopy, we estimate the binding energy of the neutral nitrogen acceptor bound biexciton (A^0_N, M) to 13.3 meV.

I. INTRODUCTION

Degenerate-four-wave-mixing experiments (DFWM) yield access to the coherent dynamics of elementary excitations in semiconductors [e.g. 1]. The dephasing times for free excitons depends on temperature, exciton density, and crystal purity. The exciton's wavefunction probes a large crystal volume and is therefore very sensitive to scattering of excitons [2], of impurity centers and of acoustic phonons [3]. However, for bound excitons due to their stronger localization dephasing times up to several hundred ps have been observed in CdSe [4] and CdS [5]. These times are still not limited by energy relaxation processes. Therefore, the idea arises if scattering of free excitons, that are created simultaneously with the excitation of (A^0, X)-complexes [5], and/or interactions with impurities determine the dephasing. In this contribution we present experiments at the nitrogen acceptor bound exciton I_1^N in ZnSe epilayers, namely time-resolved photoluminescence to determine the energy relaxation time T_1 and DFWM in the ps- and fs-region to extract the dephasing time T_2 of the bound exciton complex. Additionally, We obtain information about electronic states near the bandgap from nonlinear quantum beat spectroscopy [6] with fs excitation.

II. EXPERIMENTAL

The two samples investigated are high quality p-type ZnSe MBE-grown epilayers. The N doping is performed using a plasma source resulting in a net acceptor concentration below $3 \cdot 10^{16} \text{ cm}^{-3}$ derived from CV profiling. The thickness of the layers are 0.96 μm and 3.8 μm with a density of $\sim 1 \cdot 10^{17} \text{ cm}^{-3}$ and $\sim 1 \cdot 10^{16} \text{ cm}^{-3}$ for nitrogen on acceptor site respectively [7]. The epilayer is glued onto glass before the GaAs substrate is removed by selective wet chemical etching [8]. Time-resolved photoluminescence is carried out with time correlated single photon counting using a dye laser as excitation source (2ps pulsewidth) which is synchronously pumped by a frequency tripled active modelocked Nd:YAG laser. The photoluminescence is detected by a MCP-photomultiplier in conjunction with a subtractive double monochromator. The DFWM measurements are performed with a frequency doubled passive modelocked Ti:Saphir laser (Coherent model MIRA 900) providing pulses of 1.5 ps or 150 fs optional. With fs excitation the DFWM-signal is spectrally resolved by a double monochromator and detected time-integrated by an OMA-system. With ps-excitation the signal is detected time-integrated by a photodiode in 'lock-in' technique.

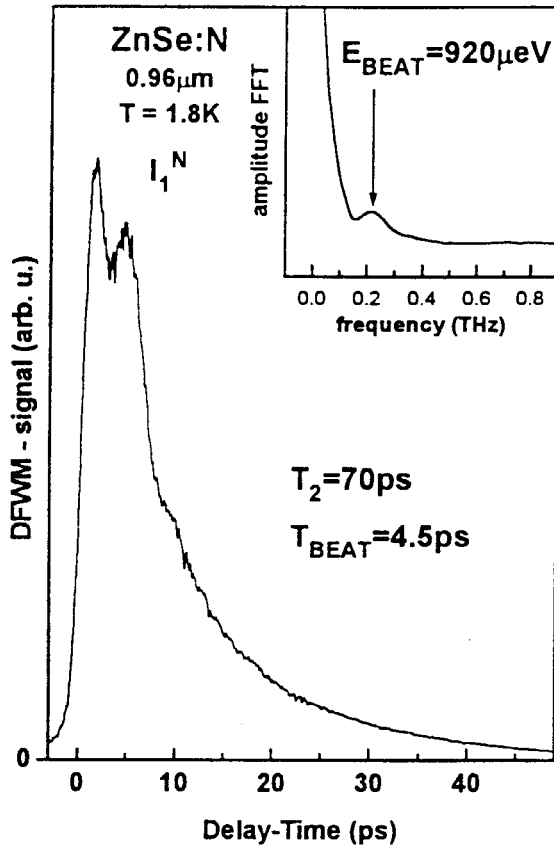


Fig. 1: DFWM-transient of the I_1^N under ps-excitation.

III. EXPERIMENTAL RESULTS

To determine the energy relaxation time T_1 of the (A_N^0, X) -complex we carried out time-resolved photoluminescence. For the ZnSe:N samples without GaAs-substrate we found a rise time below 10ps and a double exponential decay with time constants $\tau_1 = 600$ ps and $\tau_2 = 1200$ ps for the I_1^N -LO-luminescence under resonant excitation. These values are about 3 times longer than in ZnSe/GaAs samples.

The dephasing time T_2 of the (A_N^0, X) -complex can be measured by DFWM. Fig.1 depicts the DFWM transient under ps excitation of the I_1^N line in the 0.96 μm sample. We observe a decay time of 17 ps yielding $T_2 = 70$ ps with the reasonable assumption of inhomogeneous broadening. Due to the energy spread of the exciting ps-pulse both the light-hole- ($I_{1^{lh}}^N$) and heavy hole- ($I_{1^{hh}}^N$) - component of the strain split I_1^N -line [7] separated by 920 μeV are excited. Therefore, we find a beating of the signal with the corresponding beat frequency that was extracted from a Fourier transformation of the transient (inset of Fig. 1).

Table 1: Beatfrequencies and corresponding energy distances for the $I_{1^{hh}}^N$ in ZnSe

ZnSe:N I_1^N	0.96 μm				
beatfrequ. (THz)			1.38	1.86	2.54
energy dist. (meV)			5.7	7.7	10.5
transition			I_2	$I_1^{M?}$	X_{hh}
	3.8 μm				
beatfrequ. (THz)	0.68	0.92	1.14	1.87	2.57
energy dist. (meV)	2.8	3.8	4.7	7.7	10.5
transition	$I_1^{N'}$	$I_1^{N''}$?	$I_1^{M?}$	X_{hh}

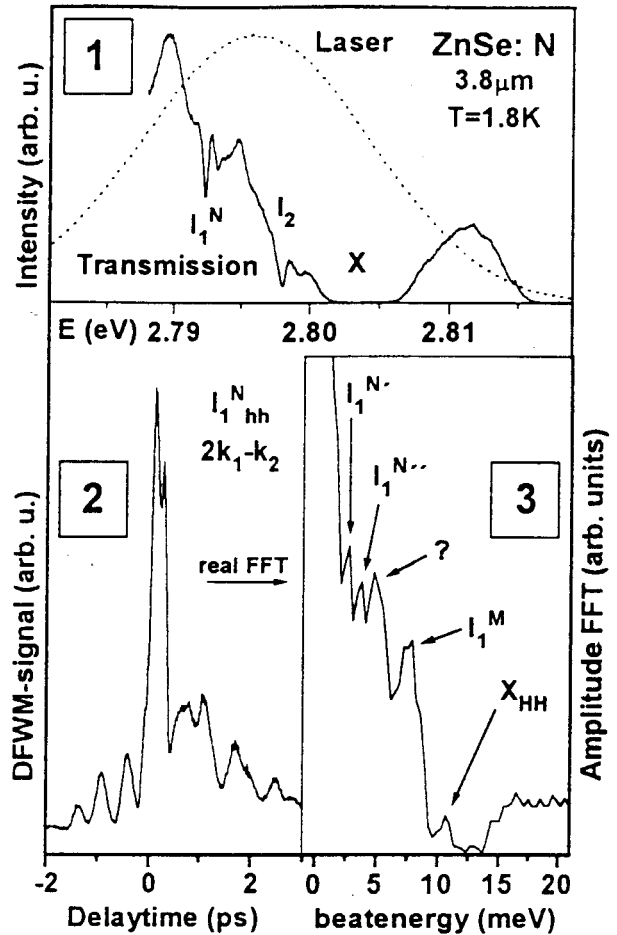


Fig. 2: DFWM-signal at the $I_{1^{hh}}^N$ -line under fs excitation. For explanation see text.

1).

In Fig. 2 the investigation is extended to broadband fs excitation. Part 1 compares the linear transmission of the 3.8 μm thick sample and the exciting laser pulse (dashed curve). Part 2 shows a typical beat structure in the DFWM-transient recorded at the $I_{1^{hh}}^N$. Here, we find that the dephasing time of about 70 ps (Fig.1) for the I_1^N is

drastically shortened with the fs excitation. Since the transient is recorded at the I_1^N -line we only observe beats where the (A_0^N, X_{hh}) -complex takes part in. To extract the beatfrequencies we perform a Fourier analysis of the signal (Part 3). For the investigated crystals Table 1 lists some of the beatfrequencies and the transitions lying at the corresponding energy distances apart from the I_1^N -line. The beatenergies of 2.8 and 3.8 meV ly close to the (A_0^N, X) -resonance where excited states of the complex are expected. The energetic positions of the neutral donor bound exciton emission I_2 and the free exciton transition X_{hh} are represented by the beatenergies 5.7 meV and 10.5 meV respectively. The beatenergy of 7.7 meV corresponds to an energetic position where the radiative recombination I_1^M of an acceptor bound biexciton is expected. The broad peak between 15 and 20 meV in the fourieranalyzed spectrum (Fig. 2 Part 3) indicates the beating of the I_1^N with a polarization generated between the $X_{n=1}$ and $X_{n=2}$ states.

DFWM-transients of the I_1^N are plotted in Fig. 3 for different detunings δE from the I_1^N peak position. For the 0.96 μm sample we observe a phase shift of π of the I_1^N - X_{hh} -beats passing the resonance indicating a polarization interference of the involved states [9]. The 3.8 μm sample shows a rather small phase shift of the I_1^M - I_1^N -beats as expected from a quantum beat system [9].

IV. DISCUSSION

The time-resolved luminescence measurements show that the decay times are strongly reduced in the ZnSe/GaAs heterostructure compared to the lifted epilayer glued onto glass. The interface opens up competing nonradiative relaxation channels due to a high strain induced defect concentration. The decay time of the I_1^N -transition in the epilayer without GaAs-substrate are to our knowledge the longest reported in the literature for (A_0^N, X) -complexes in ZnSe [e.g. 10] confirming the high quality of the samples. The double exponential decay of the transitions may be explained by the simultaneous detection of two spectrally unresolved lines with different oscillator strength or inhomogeneity of the layers. Nevertheless, the energy relaxation time of the (A_0^N, X) -complex amounts at least to $T_1 = 600$ ps in the 0.96 μm sample.

Also a long dephasing time almost limited by energy relaxation is expected for a strongly localized system as an acceptor bound exciton [4,5], we observe a drastic reduction of T_2 for the I_1^N in our epilayers. Evaluation of the compensation in the investigated samples [7] yields a degree of ~60% compensation of the incorporated nitrogen on acceptor site. This results in a minimum impurity concentration of $\approx 2 \cdot 10^{17} \text{ cm}^{-3}$ corresponding to a minimum distance of about 17nm between the impurity sites. The extension of the wavefunction of the (A_0^N, X) -complex amounts to about 2.4 nm (average value for the X_{lh} and X_{hh} component). Additionally, the recharging of charged donors and acceptors results in the creation of free carriers and, therewith, free excitons that reduce the dephasing time of the (A_0^N, X) -complex due to scattering with the bound exciton complexes [5]. From that we conclude that both impurity interactions and scattering with free excitons are responsible for the dephasing time of the (A_0^N, X) -complex. As can be seen from Fig. 2 Part 2 the dephasing rate is

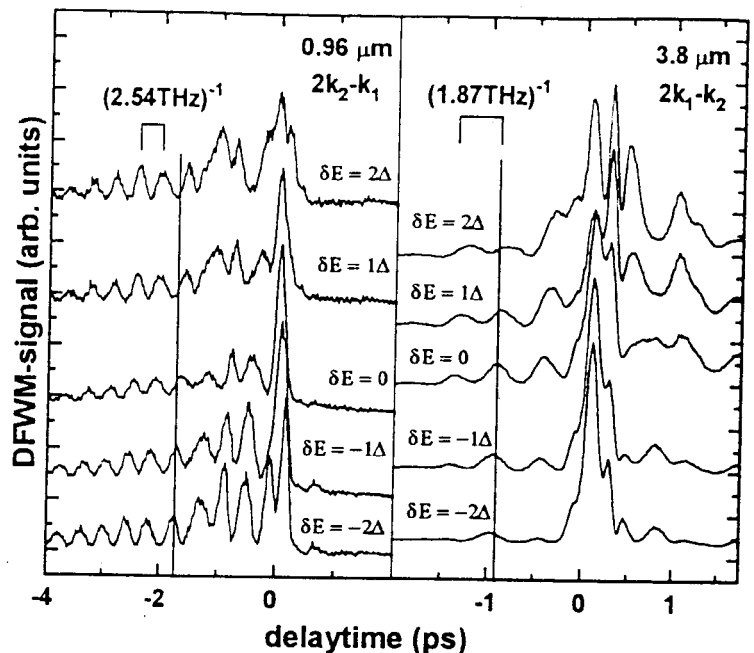


Fig. 3: DFWM-transients recorded for different detunings $\Delta = 136 \mu\text{eV}$ from the I_1^N -line in ZnSe-epilayers.

further increased with fs excitation. We attribute this to scattering with the enlarged number of free excitons that are directly created by the broadband laser pulse.

The rich beat structure in the recorded transients allows for the identification of interfering states. The 3.8 μm sample reveals two small beatenergies 2.8 and 3.8 meV that we assign to interferences of the (A^0_N, X_{hh}) -state with excited states of the complex. For the 0.96 μm sample the beatenergies of 5.7 and 10.5 meV unambiguously identify the I_2 - and X_{hh} -resonances as participating in the beats.

Both samples exhibit a strong beat amplitude at 7.7 meV. The corresponding energy distance leads to an energy lying between the transitions of the I_2 - and X_{hh} -resonance. In this energy region in CdS the radiative recombination I_1^M of an acceptor bound biexciton (A^0, M) has been reported [11]. Equivalent to our measurements in ZnSe, a quantum beat behaviour has been found in CdSe too [6]. Therefore we propose for the 7.7 meV peak a beating in the coherently driven system $A^0 + h\nu_1 \rightarrow (A^0, X)$ and $(A^0, X) + h\nu_2 \rightarrow (A^0, M)$ [9]. We estimate a binding energy for the (A^0, M) -complex of $E_{xm}^b = (10.5 + (10.5 - 7.7)) \text{ meV} = 13.3 \text{ meV}$ in ZnSe. Here the binding energy is given with respect to the state formed by two free excitons.

In principle quantum beats should be expected from the three level system formed by the crystal ground state, the (A^0_N, X_{hh}) -state and the free exciton state X_{hh} . However, we observe a polarization interference in our samples as we conclude from the π -phase shift in the beats (Fig.3). Only a small peak amplitude is observed for the beatenergy of 7.7 meV in the 3.8 μm sample, whereas the 0.96 μm sample shows a strong beat amplitude. We attribute this to the higher density of (A^0_N, X) -complexes in the 0.96 μm sample. The generation rate of free excitons should be the same in both layers per unit volume but is highest at the surface facing the incoming pulse. The appearance of polarization interference for the (A^0_N, X_{hh}) - X_{hh} -beats indicates a small coherence volume of the free exciton [12] but may in the case of optically thick samples also due to a spatial separation of free and bound excitons.

V. CONCLUSION

With time-resolved luminescence and DFWM we determined the energy relaxation and dephasing times of the (A^0_N, X) -complex in p- conductive ZnSe to be $T_1 \geq 600 \text{ ps}$ and $T_2 = 70 \text{ ps}$. Additionally we observed nonlinear quantum beats involving the (A^0_N, X_{hh}) -complex, some of its excited states, and the (D^0, X) -complex. We found polarization interference for the (A^0_N, X_{hh}) - X_{hh} -system and quantum beats in the three level system formed by A^0 , (A^0_N, X) and (A^0_N, M) . The binding energy of the neutral nitrogen acceptor bound biexciton (A^0_N, M) in ZnSe is $E_{xm}^b = 13.3 \text{ meV}$.

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