Formation and phase relaxation of negatively charged excitons in ZnSe single quantum wells

H. P. Wagner*
Institut für Physik, TU Chemnitz, D-09107 Chemnitz, Germany

H.-P. Tranitz and R. Schuster
Institut Physik II, Universität Regensburg, D-93040 Regensburg, Germany
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We investigate the formation, interaction, and dephasing of negatively charged excitons (trions) in $ZnSe/Zn_{0.9}Mg_{0.1}Se$ single quantum wells by polarization, intensity, and temperature dependent spectrally resolved transient four-wave mixing. The trion transition shows a binding energy of 2.8 meV and is discriminated from the biexciton by its polarization dependence. The coherent dynamics of the four-wave mixing response is in fair agreement with calculations based on extended optical Bloch equations. Temperature dependent measurements exhibit a significant enhancement of the exciton dephasing below 40 K due to the presence of trions and incoherent electrons which are optically excited from the GaAs substrate and captured by the quantum well. [S0163-1829(99)11347-X]

The existence of trions which are negatively or positively charged excitons was discussed by Lampert[1] already in 1958. According to calculations of Munschy[2] the binding energy of the second electron in a negatively charged exciton reaches values of 1 meV in bulk ZnSe. In the two-dimensional (2D) limit an increase of the binding energy by a factor of 10 is expected[3] making ZnSe quantum wells (QW's) appropriate systems to study these quasiparticles. Extensive investigations have already been reported on the formation and the behavior of negatively charged excitons by applying external magnetic[4–6] or electric fields[7] using various II-VI and III-V QW structures. The electrons which bind to photoexcited electron-hole pairs were provided by doping,[4] electrical injection,[5,6] or tunneling.[7] Recently, the recombination of trions in GaAs QW's was investigated by time-resolved photoluminescence (PL) experiments.[8] There are, however, less investigations on the interaction and dephasing of trions in single QW's using coherent spectroscopic methods.[9,10]

In this paper we report on polarization, intensity, and temperature dependent, spectrally resolved four-wave-mixing (FWM) experiments on undoped $ZnSe/Zn_{1-x}Mg_xSe$ single QW's (SQW's) showing that the trion formation is due to electrons which are photoexcited from the GaAs substrate into the QW. The measurements further demonstrate a significant enhancement of the exciton dephasing rate due to the presence of QW electrons and trions.

The investigated samples were pseudomorphically grown on (001) oriented GaAs by molecular beam epitaxy. The samples consist of a 10 nm wide ZnSe SQW sandwiched between two $Zn_{0.9}Mg_{0.1}Se$ barriers, with varying layers between the QW and GaAs substrate. Sample A has a 20 nm thick ZnSe buffer layer on the GaAs and 30 nm thick barriers. Sample B differs from sample A by the missing buffer layer and sample C from B by the reduced $Zn_{0.9}Mg_{0.1}Se$ barrier thickness of 20 nm. A detailed description of the growth process and the sample characterization by optical and structure methods is given elsewhere.[11]

The four-wave-mixing experiments were performed in backscattering geometry using a two-beam self-diffraction configuration. A frequency-doubled, mode-locked Ti-sapphire laser was used as excitation source, producing 100 fs pulses [full width at half maximum (FWHM) irradiance] of 22 meV spectral width at a repetition rate of 82 MHz. The focus diameter of the pulses at the $1/e^2$ intensity on the sample was 100 μm. The polarizations of the two incident pulses with the directions $\mathbf{k}_1$ and $\mathbf{k}_2$ and the mutual delay time τ have been adjusted to cocircular (σ^+,σ^+) as well as linear with relative angles of 0° ($\uparrow\uparrow$) and 90° ($\uparrow\rightarrow$). The first (second) symbol in the parentheses indicates the polarization of the $\mathbf{k}_1$ ($\mathbf{k}_2$) pulse, respectively. The FWM signal in the reflected $2\mathbf{k}_2-\mathbf{k}_1$ direction was time-integrated and spectrally resolved by a combination of a spectrometer and an optical multichannel analyzer. The sample was kept in a helium cryostat permitting temperature-dependent measurements. If not otherwise mentioned, the experiments were carried out at a temperature of $T=15$ K.

The spectrally resolved FWM signals of sample C at a delay time $\tau=0$ ps for various excitation intensities and collinear polarized fields ($\uparrow\uparrow$) is shown in Fig. 1(a). The center frequency of the excitation pulse was set to 2.812 eV, in order to avoid continuum contributions but resonantly excite the $11h$ $1s$ heavy-hole exciton X. Besides the FWM X signal, a low energy peak (T) appears, that is attributed to a negatively charged exciton transition by the following considerations.

The energetic distance of the T line to the X resonance amounts to 2.8 meV. This value is too small to fit with binding energies of donor bound excitons which have been determined by photoluminescence to $E_B=(6\pm1)$ meV in similar $ZnSe/Zn_{1-x}Mg_xSe$ structures.[12] Furthermore the T line FWM peak intensity shows a nonlinear increase even for high pulse intensities of 3.5 MW/cm^2, whereas saturation effects of the FWM signal would be expected in case of impurity bound exciton transition. Therefore these exciton complexes are dismissed as origin of the T line which is further supported by a comparison of the FWM spectra of samples A, B, and C. Figure 1(b) shows the FWM spectra normalized to the exciton X signal at zero delay time excited

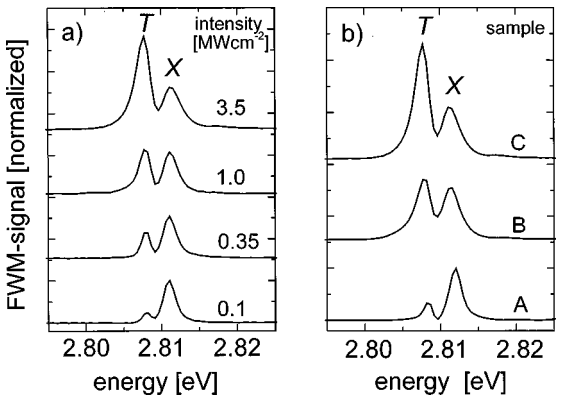

FIG. 1. (a) Normalized FWM spectra at a delay time $\tau=0$ ps of sample C ($d=20$ nm) excited resonantly at the heavy hole $11h$ exciton transition X at various excitation intensities (labeled). The T line indicates the trion transition. (b) Normalized FWM spectra at $\tau=0$ ps of sample A ($d=50$ nm), B ($d=30$ nm), and C ($d=20$ nm) at an excitation intensity of 3.5 MW/cm^2.

at an intensity of 3.5 MW/cm^2. With decreasing distance d between GaAs substrate and ZnSe single QW the T line increases compared to the X signal which is in contrast to an impurity bound exciton signal since the amount of impurities decreases with decreasing total thickness of the quantum well structure. From these observations the T line is attributed to the formation of negatively charged excitons where the incoherent electrons are provided by optically excited GaAs valence band electrons. The excess energy of optically excited electrons in the GaAs substrate amounts to about 1.2 eV, much more than conduction band offset of about 0.12 eV at low temperature.[13] A fraction of photoexcited electrons thus can escape from the GaAs into the ZnSe QW, where they accumulate until an equilibrium concentration is reached due to the buildup of a reverse electric field by the charge density. These excess electrons in the QW lead to the formation of trions. The trion FWM signal increases with decreasing distance d due to an increasing equilibrium concentration of excess electrons.

The identification of the T line is further strengthened by polarization dependent FWM measurements which clearly distinguish the trion response from the formation of biexcitons (BIF) with comparable binding energies.[12] According to the Pauli exclusion principle bound biexcitons are only formed by excitons of opposite spin. Therefore the biexciton induced FWM signal can be suppressed by using circular polarized light. The FWM spectra of sample A at a negative delay time of $\tau\approx-0.2$ ps ($\mathbf{k}_2$ before $\mathbf{k}_1$) for cocircular (σ^+,σ^+), colinear ($\uparrow\uparrow$), and cross-linear ($\uparrow\rightarrow$) polarized laser pulses at an intensity of 0.1 MW/cm^2 are displayed in Fig. 2. The intensity of the T line is comparable for (σ^+,σ^+) and ($\uparrow\uparrow$) polarized fields, excluding a biexcitonic origin of the T transition. Instead, a second signal, denoted as XX, is observed, which vanishes in the (σ^+,σ^+) configuration. In the cross linear ($\uparrow\rightarrow$) configuration the intensity of the T line is strongly decreased together with the signal of the X resonance due to the lack of excitation induced dephasing (EID).[14] The XX signal is not affected, as expected for a biexciton induced signal. The XX signal is thus attributed to BIF, and a biexciton binding energy of $E_{XX}=5.5$ meV is deduced.

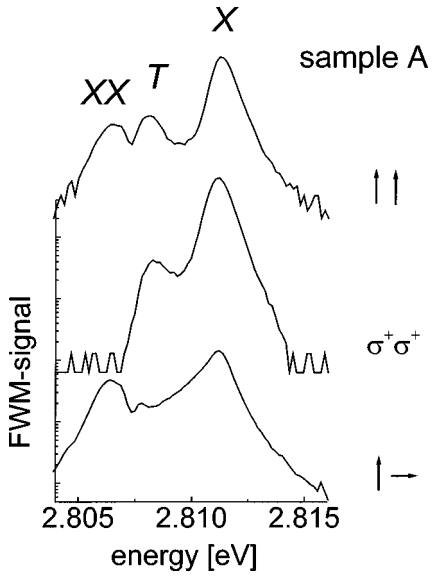

FIG. 2. FWM spectra from sample A ($d=50$ nm) for cocircular (σ^+,σ^+), colinear ($\uparrow\uparrow$), and cross-linear ($\uparrow\rightarrow$) polarized laser pulses recorded at a delay time of $\tau\approx-0.2$ ps. The excitation intensity is 0.1 MW/cm^2.

The delay-time dynamics of the spectrally resolved FWM for (σ^+,σ^+) polarized fields is given in Fig. 3(a) at the spectral positions of the exciton X transition ($\hbar\omega_X$), the trion T transition ($\hbar\omega_T$), and at frequencies $\hbar\omega_T\pm\delta$ with a detuning $\delta=0.8$ meV. The FWM traces show pronounced beats at the trion resonance and at $\hbar\omega_T\pm\delta$ with a time period $T_P=1.5$ ps corresponding to the observed trion binding energy of $E_T=2.8$ meV. Furthermore, a phase shift of the beats over the trion resonance for positive and negative delay times is observed.

To evaluate these results more quantitatively, we modeled the FWM response by optical Bloch equations (OBE) of two independent homogeneously broadened two level systems (as type II in Ref. 15). An analysis of the interaction-induced processes and its relative importance to the FWM signal has shown that the EID contribution dominates the FWM signal

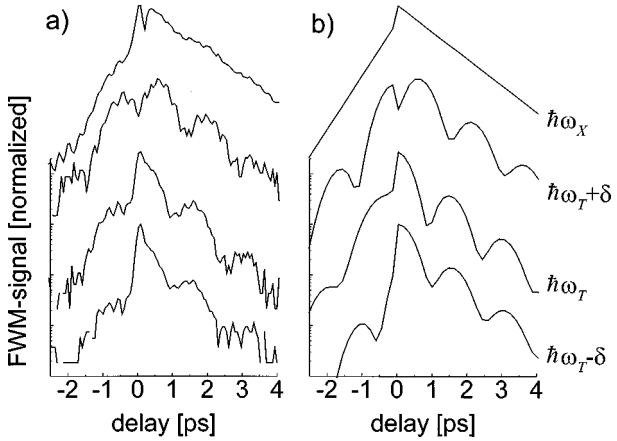

FIG. 3. (a) FWM traces for (σ^+,σ^+) polarized fields at the heavy-hole $11h$ X resonance ($\hbar\omega_X$), the trion T transition ($\hbar\omega_T$), and at the frequencies $\hbar\omega_T\pm0.8$ meV. (b) Calculated FWM spectra at the same spectral positions based on an OBE including EID using Eqs. (1) and (2).

in cocircular (σ^+,σ^+) and colinear $(\uparrow\uparrow)$ configuration while local field effects (LFE) play a subordinate role.[16] The OBE are thus extended to encompass EID, but not LFE. The independent two-level systems are the $11h$ exciton state (X transition) with its initially occupied ground state, and the trion singlet state (T transition) with its initially occupied ground state of the incoherent QW electron. The resonance energies $\omega_{X(T)}$ and dephasing rates $\gamma_{X(T)}$ given by $\Omega_{X(T)}=\omega_{X(T)}-i\gamma_{X(T)}$ are determined from the obtained FWM spectra and traces [Fig. 2 and Fig. 3(a)]. The dephasing rates $\gamma_{X(T)}=\gamma_{X(T)}(n_X=0)+\sigma^{(\prime)}n_X$ used in the EID process were taken to depend only on the spatial modulation of the exciton density n_X of created $11h$ excitons. The total density of created negatively charged excitons n_T plus remaining incoherent QW electrons n_e keeps constant $n_T+n_e=n^-$ in the FWM process. Therefore, assuming similar electron-exciton and trion-exciton scattering rates, the spatial modulation of the trion and incoherent electron density does not contribute to EID. The third-order response can be solved analytically in the perturbative regime, and the calculated Fourier transformed third-order polarization for infinitely short cocircular (σ^+,σ^+) polarized excitation pulses for positive delay reads

$$P^{(3)}(\omega,\tau>0)\propto\Theta(\tau)N\mu_X^4\exp(i\Omega_X^*\tau)\exp(i\omega\tau)\left[\frac{2}{(\omega-\Omega_X)}+iN\sigma\frac{1}{(\omega-\Omega_X)^2}\right]+\Theta(\tau)N'\mu_T^2\exp(i\omega\tau)$$
$$\times\left[\mu_T^2\exp(i\Omega_T^*\tau)\frac{2}{(\omega-\Omega_T)}+iN\sigma'\mu_X^2\exp(i\Omega_X^*\tau)\frac{1}{(\omega-\Omega_T)^2}\right]. \quad (1)$$

For negative delay the third-order polarization is given by

$$P^{(3)}(\omega,\tau<0)\propto i\Theta(-\tau)N^2\sigma\mu_X^4\exp(2i\Omega_X\tau)\frac{1}{(\omega-\Omega_X)^2}+i\Theta(-\tau)NN'\sigma'\mu_X^2\mu_T^2\exp(i\Omega_X\tau)\exp(i\Omega_T\tau)\frac{1}{(\omega-\Omega_T)^2}. \quad (2)$$

In the equations Θ is the Heaviside function. The oscillator strengths μ_X^2 and μ_T^2 were determined from the experimental FWM data to $\mu_X^2=1$ and $\mu_T^2=0.5$, where the densities of excitons N and trions N' were assumed to be equal for simplicity. The EID parameters $\sigma_X=N\sigma=7.1\gamma_X$ and $\sigma_T=N\sigma'=2\gamma_X$, were taken from the FWM intensity ratio between $(\uparrow\uparrow)$ and $(\uparrow\rightarrow)$ configuration. The calculated FWM traces which are proportional to $|P^{(3)}(\omega,\tau)|^2$ are plotted in Fig. 3(b) at the spectral positions corresponding to the traces in Fig. 3(a). Besides the slight modulation at the exciton X transition, indicating a weak EID due to the trion/electron density which has been neglected, the calculations based on this simple model show fair agreement to the experimental data and reproduce the phase shifts of the beat.

The existence of QW electrons and trions not only affects the coherent dynamics and FWM signal intensity but also leads to a decrease of the exciton decay time as a consequence of exciton-electron scattering. The exciton and trion homogeneous linewidths, given by $\Gamma=2\hbar/T_2$, are thus a probe for the excess electron concentration. With increasing distance d between single QW and GaAs substrate, the linewidths are decreasing (inset of Fig. 4), in agreement with the intensity of the trion signal in Fig. 1(b). With increasing temperature the intensity of the T line diminishes and vanishes at about $T=50$ K. This behavior is mirrored in the development of the homogeneous linewidth of the X resonance and the T transition as demonstrated in Fig. 4. At $T=15$ K the homogeneous linewidth of the exciton transition has a value of $\Gamma=1.84$ meV. With increasing temperature this value decreases by a factor of 2 until a minimum at $T=55$ K is reached. The temperature dependence of the trion homogeneous linewidth shows a similar behavior but starts at a value of $\Gamma=2.54$ meV. Above $T=50$ K the T line vanishes and the exciton linewidth begins to increase due to the onset of exciton-LO-phonon scattering.[12] The observed results are interpreted in the following. The scattering between incoherent electrons, negatively charged excitons, and neutral excitons is reflected in the significantly enhanced homogeneous linewidth of the exciton FWM signal at $T=15$ K.[17] With rising temperature, the equilibrium excess carrier concentration decreases due to thermal activation over the barrier which has a conduction band offset of about 25 meV.[11] Therefore the exciton dephasing is reduced. At temperatures above $T=50$ K the excess carrier concentration is so low that a trion FWM signal is no longer observable.

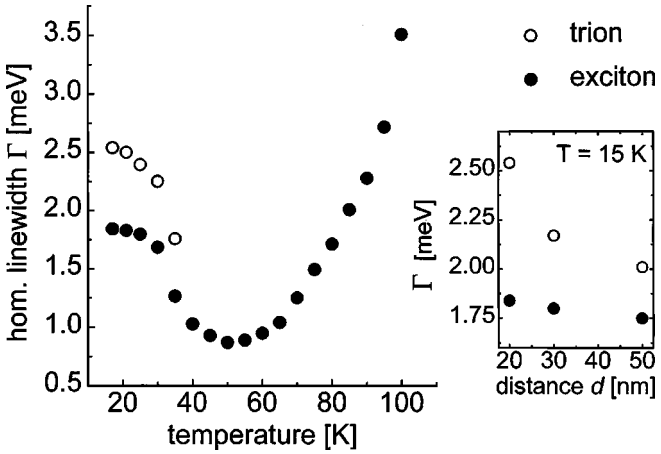

FIG. 4. Homogeneous linewidth of the X resonance and trion T transition as a function of the lattice temperature T obtained from sample C. The excitation intensity was 3.5 MW/cm^2. The inset shows the homogeneous linewidths of the X and T line at $T=15$ K of samples A, B, and C as a function of the distance d between ZnSe single QW and GaAs substrate.

In conclusion, we have identified the formation of trions in $ZnSe/Zn_{1-x}Mg_xSe$ single quantum wells by means of intensity-dependent spectrally-resolved degenerate FWM on samples with varying distance d between the ZnSe single QW and GaAs substrate. The observed trion transition T is clearly distinguished from the biexciton induced FWM signal XX by its polarization dependency. A trion binding energy of 2.8 meV is found. The coherent dynamics of the FWM response for cocircular polarized fields is in reasonable agreement with calculations based on the optical Bloch equations which are extended by excitation-induced dephasing from the modulated exciton density. The exciton homogeneous linewidth is dominated at 15 K by exciton-electron scattering. With rising temperature the excess electron density is reduced due to thermal activation and a decrease of the trion peak intensity and exciton homogeneous linewidth is observed.

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*Author to whom correspondence should be addressed. Present address: Universität Regensburg-Physik II, Universitätsstraße 31, D-93040 Regensburg, Germany. FAX: 49 9419434226. Electronic address: Hans-Peter.Wagner@physik.uni-regensburg.de HP.Wagner@physik.tu-chemnitz.de

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