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Observation of antibound states for exciton pairs by four-wave-mixing experiments in a single ZnSe quantum well

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We have employed spectrally resolved, subpicosecond transient four-wave-mixing techniques to identify and to study the four-particle ''antibound states'' associated with excitonic molecules in a binary ZnSe single quantum well. Previously, the existence of robust bound biexcitons have been observed in this wide band-gap semiconductor heterostructure, including a density regime where optical gain is dominated by the molecular states. We employ selective circular polarization excitation to suppress the bound (ground state) exciton-pair state contribution and find a spectrally distinct and isolated feature emerging approximately 3.5 meV higher in photon energy than the $n=1$ heavy-hole exciton transition. The new resonance is distinct only in the negative time delay regime, and is interpreted as a manifestation of coherent four-particle correlated states within the biexciton continuum. [S0163-1829(98)51736-5]

While excitons and their excited states have been thoroughly investigated in many semiconductors, important questions remain about their many-body interactions, especially those that involve complexes such as biexcitons, triexcitons, and so on. Biexcitons have been for several years studied in GaAs quantum wells (QW's),[1] with theoretical[2] and experimental[3] work yielding new insight with unexpected nuances imposed by the four-particle correlations, in particular to four-wave-mixing (FWM) probes. Elsewhere, Ikezawa *et al.*[4] have recently reported on excited biexciton and triexciton states in CuCl quantum dots. The II-VI semiconductor QW's have also been a source of rich exciton physics, including the demonstration that excitonic molecules in their ground state can support a very large optical gain (10^5 cm^{-1}) at cryogenic temperatures.[5,6] In zinc-blende semiconductors, the bound pairs of excitons (molecules in their ground state) have a total angular momentum of $J=0$, as they are formed from heavy-hole (HH) excitons of opposite spins. In a binary ZnSe the molecular binding energy has been measured to be $\Delta E_b = 5 \pm 0.5$ meV, while additional localization effects in the $Zn_xCd_{1-x}Se$ random alloy increase the effective binding, measured relative to the exciton, to nearly 10 meV.[7] Considerations based solely on basic rules applicable to angular momentum addition provide the basis for the optical excitation schemes for the observation of the molecular ground state. The same rules also predict optical access to an ''antibound'' state, in the simplest picture where the excitation spectrum of the true correlated four-particle state is replaced by a state with a repulsive energy ΔE_a. This state, unstable in the sense that its binding energy has a negative value, possesses a total angular momentum of $J=2$ ($J_m=-2, 0, 2$), and is made up of two excitons of parallel spins. In reality, the concept of this type of an antibound state is too simplistic due to many-body Coulomb correlations; nonetheless we employ it as a schematic starting point in our discussion. In fact, as shown in the work by Schäfer *et al.*,[2] a full description of the problem requires the proper accounting of the biexciton continuum states that couple to coherent nonlinear polarizations, in order to fully account for the four-particle Coulomb correlations. From a wholly different point of view, the presence of excited biexciton states has been inferred in recent pump-probe experiments on CuCl quantum dots and theoretically considered within the framework of weakly correlated, confined exciton-pair states.[4] As for II-VI semiconductors, in their study of excitons and biexcitons in $Zn_xCd_{1-x}Se$ QW's Häupl *et al.* noted a spectral asymmetry in the FWM signal at the HH exciton resonance and suggested this feature as a possible indicator of an antiboundlike molecular state.[8] In this paper, we report a clear experimental observation of these types of ''antibound states'' in a single ZnSe QW from spectrally resolved, transient, degenerate FWM measurements.

Four-wave mixing has been the technique of choice for exploring the dynamics of coherently excited exciton-biexciton systems in both III-V and II-VI semiconductors, both in the bulk and quantum wells. The study of the ZnSe binary II-VI semiconductors QW offers advantages in this context since, in addition to the intrinsically large exciton oscillator strengths, sub-meV linewidths of the lowest exciton state have been measured in quality samples.[6] Hence, both the exciton and biexciton states, as well as their interactions, can be studied with high spectral clarity and precision. Furthermore, the absence of a significant inhomogeneous broadening due to alloy compositional fluctuations, such as encountered in the more strongly type-I $Zn_xCd_{1-x}Se$ QW, reduces the rates of dephasing that can significantly diminish the observation of coherent excitations such as those discussed below.

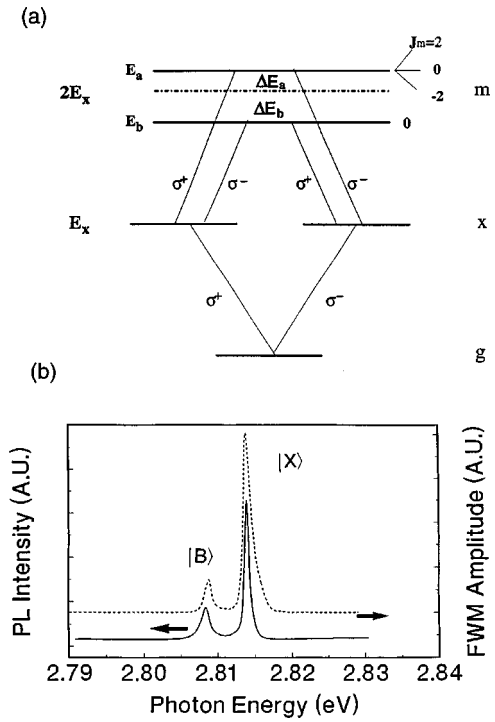

FIG. 1. (a) Schematic five-level model diagram with relevant angular momentum and optical transition rules for the one- and two-exciton system; (b) a comparison between the PL and the FWM spectra for a ZnSe SQW at $T=10$ K (latter taken at a time delay of $\tau=0.66$ ps), showing the coincidence of the positions for the excitonic ($|X\rangle$) and biexcitonic ($|B\rangle$) resonances.

As a schematic guide for introducing the relevant energy scales for the experiments discussed below. Fig. 1(a) shows a five-level model of energy level diagram featuring exciton and molecular states relative to the crystal ground state in a zinc-blende semiconductor adapted from Ref. 8. (In a ZnSe quantum well, the $k=0$ degeneracy between the HH and light-hole (LH) valence states is lifted and only the HH states are included in the figure.) For an incident optical wave vector $\mathbf{k}_z$ perpendicular to the QW layer plane, only transitions with $\Delta J_z=\pm 1$ are dipole allowed, driven by oppositely circularly polarized fields, leading to the generation of $\sigma+$ and $\sigma-$ excitons at an energy E_x that carry a total angular momentum $J=1$ [with $J_z=+1$ ($\sigma+$) or $J_z=-1$ ($\sigma-$)]. By extension, direct optical access (by electric dipole transitions) to the states of exciton pairs is only possible for $J=2$ ($J_z=+2,0,-2$) and $J=0$.[9] the $J=0$ states are the familiar bound excitonic molecules at an energy E_b, being composed of two excitons with opposite z component of angular momentum, i.e., in antispin configuration. In the hydrogenic molecular analog and neglecting (the crucial) many-body interactions, the $J=2$ ($J_z=+2,0,-2$) states correspond to a single antibound two-exciton state at an energy E_a with parallel-spin orientation and with a repulsive interaction between the two excitons that leads to a negative binding energy, labeled as ΔE_a in Fig. 1(a). Of course, as already noted, this picture is oversimplified and consequently omits key pieces of physics that originate from the interplay of many-electron correlations within the biexciton continua with the electromagnetic polarizations as shown in Ref. 2. The presence of a dense electron-hole (e-h) population or polarization due to these principal excitations in a semiconductor quantum well gives rise to interparticle interactions that both enable their detection (finite $\chi^{(3)}$) and give an opportunity to study such interaction in FWM spectroscopy in the coherent regime. In the spirit of Fig. 1(a), the optical fingerprint of ''antibound'' states should appear on the higher energy side of the corresponding HH $n=1$ exciton resonance.

The ZnSe single QW samples for this study were grown by molecular-beam epitaxy on lattice-matched GaAs substrates and epitaxial buffer layers. The configuration for the pseudomorphic II-VI material was a ZnSe/Zn(S,Se)/(Zn,Mg)(S,Se) separate confinement structure, which has facilitated the study of optical gain and lasing by biexcitons in these samples as reported previously.[6] The active region was formed by a 75-Å-thick QW, surrounded by 1000-Å-thick Zn(S,Se) barrier and optical waveguide layers, cladded by 0.5-mm-thick (Zn,Mg)(S,Se) optical confinement layers. The conduction-band offset for ZnSe/Zn(S,Se) is relatively modest so that in terms of the binding energy, our excitons have a mixed two-dimensional–three-dimensional (2D)-(3D) character.[6] The GaAs substrate and buffer layers were subsequently removed by wet chemical etching. The absence of alloy compositional fluctuations, such as encountered in the more frequently studied ternary (ZnCd)Se QW's, leads to the presence of a narrow, intense $n=1$ HH exciton resonance, readily observed, e.g., in a single pass transmission experiment with a peak absorption coefficient of $\alpha=2\times10^6$ cm^{-1} and a full width at half maximum linewidth of about 0.5 meV. The HH exciton is very well isolated, by more than 10 meV, from both the excited HH exciton states and the $n=1$ LH excitons, as well as their continuum states (by about 25 meV). As shown below, this makes it possible to observe unambiguously both the biexcitonic ground and higher excited (''antibound'') correlated pair states. We note that the spectral sharpness of these transitions in our II-VI system makes up for the considerably larger energy scale associated with excitons, e.g., in the cuprous halides in terms of the clarity of the spectroscopic observations.

We performed spectrally resolved, transient four-wave mixing experiments on the single quantum well (SQW) ZnSe samples by using the frequency doubled output of a Kerr-lens mode-locked Ti:sapphire laser (150-fs pulsewidth, spectral width of about 20 meV, and a 76-MHz repetition rate). The laser beam was divided by a beam splitter, with one beam passing through an adjustable time-delay line. The two beams were focused on the sample with an angle less than 5° from the normal to the QW layer plane. The FWM signal was observed in the background-free direction $\mathbf{2k}_2-\mathbf{k}_1$, where $\mathbf{k}_1$ and $\mathbf{k}_2$ represent the wave vectors of the pump and probe beams, respectively. Polarization control of the two beams was achieved by using both prism polarizers and quarter-wave plates. Figure 1(b) shows the photoluminescence (PL) spectrum and a representative FWM spectrum taken at a temperature $T=10$ K. The excitation level for the PL spectrum corresponds to an e-h pair density of about 5×10^{10} cm^{-2} and that for the FWM spectrum to $n\approx2\times10^{11}$ cm^{-2}. The latter density is about a factor of 5 below the estimated ''Mott density'' for excitons in the 2D limit in ZnSe. The FWM spectrum, which falls well within the spectral bandwidth of the laser, is shown for a time delay of 0.66 ps with the pump and probe beams linearly polarized (parallel configuration). In the PL spectrum, we can clearly iden-

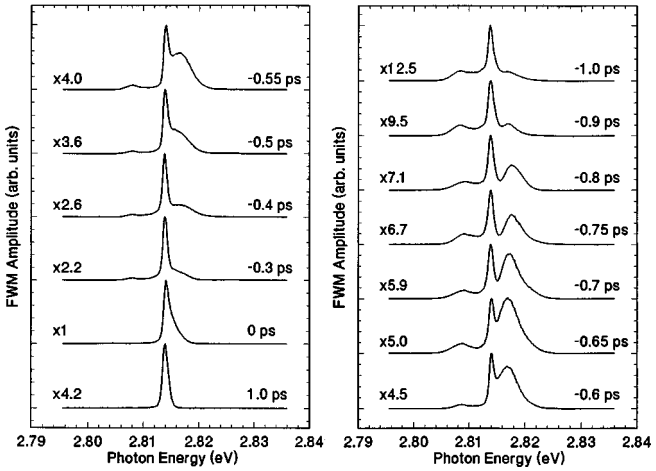

FIG. 2. Transition FWM spectra as a function of pump-probe time delay for the SQW ZnSe sample under co-circular-polarization configuration at $T=10$ K, including amplitude normalization factors. The excitation level corresponds to a pair density of $n=2\times10^{11}$ cm^{-2}.

tify two peaks, a feature at $h\omega=2.814$ eV due to radiative recombination of the HH excitons (labeled as $|X\rangle$), and a resonance at $h\omega=2.809$ eV that originates from the radiative dissociation of (bound state) biexcitons into excitons, emitting a photon with an energy of E_b-E_x (labeled as $|B\rangle$). This identification has been discussed in detail elsewhere.[6] Of course, the PL by the biexciton emission is due to an incoherent process, while that for the FWM emphasizes a coherent nonlinear polarization involving this four-particle bound state. While a perfunctory comparison of the PL and FWM line-shape features shows that the biexcitonic features are very similar, the $n=1$ HH excitonic peak width in the FWM spectrum shows a distinct asymmetry, with extra broadening on the high energy side. This observation, together with the theoretical and previous experimental arguments about the particular fingerprints of excited states for exciton pairs, prompted us to search for the manifestation of these types of states in ZnSe QW's. Since the ''antibound'' states are unstable configurations of biexcitons, such an experiment should be preferably carried out in a regime where the excitonic wave functions are fully coherent, typically in the sub-ps time domain in a transient FWM experiment.

Figure 2 shows the time-integrated FWM spectra as a function of pump-probe delay for the *co-circular-polarization* configuration at $T=10$ K. As in Fig. 1(b), the excitation conditions correspond to an equivalent electron-hole pair density of 2×10^{11} cm^{-2}. We have found that this is very nearly the optimum excitation density for maximizing the amplitude of ''antibound'' exciton pair features described next. The individual FWM spectra, which emphasize the importance of the negative time-delay regime, are displayed vertically for clarity. At zero delay, the asymmetry on the high energy side of the $n=1$ HH exciton, centered at $h\omega=2.814$ eV, is enhanced relative to the case of the conventional parallel linear polarization under the same conditions of excitation. With increasing (negative) time delay, the asymmetry becomes increasingly pronounced, and develops into two spectrally resolved resonances. For a delay of $T=-0.7$ ps, the (spectrally integrated) cross section for the higher energy feature centered at $h\omega=2.8175$ eV rivals and actually exceeds that for the exciton FWM signal. This is the

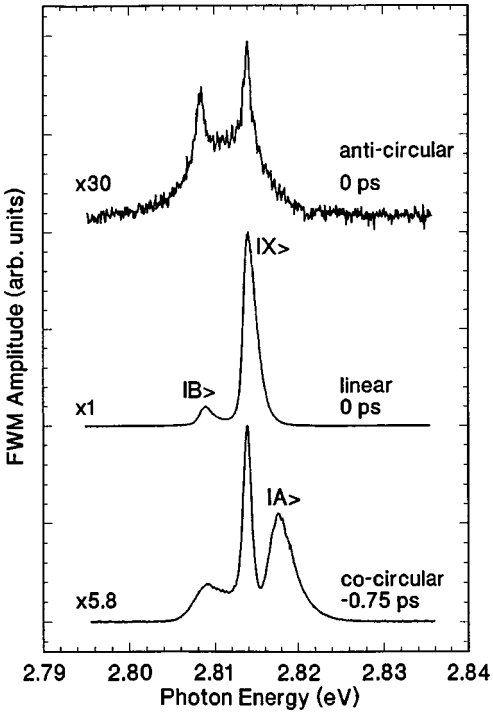

FIG. 3. A comparison of the FWM spectra measured under co-circular-polarization configuration ($\tau=-0.75$ ps) highlighting the antibound exciton-pair transition $|A\rangle$, linear-polarization configuration ($\tau=0$ ps), and anti-circular-polarization configuration ($\tau=0$ ps), all under the same conditions of excitation.

feature we interpret as a direct manifestation of the impact of the antibound states of the excitonic molecule, roughly with an effective ''repulsive'' energy $\Delta E_a=3.5$ meV relative to the excitonic transition. (Close examination of Fig. 2 shows an apparent small, time-dependent shift in the position of the peak associated with the $|A\rangle$ transition; the magnitude of the shift is, however, close to the experimental resolution.) Note how the signal decays rapidly for further increase in the negative time delay so that by $\tau=-1$ ps, it has been reduced to a level comparable to a residual contribution from the bound state of the excitonic molecule at 2.809 eV. The occurrence of the finite signal from the ground state of the excitonic molecule is, of course, contrary to the spin/orbital selection rules and is here attributed to the less than 100% purity of circular polarization in our experimental setup. (The polarization impurity arises from the finite misalignment of the quarter-wave plates and the spectral breadth of the Ti:sapphire laser so that finite dispersion in the birefringence in the quarter-wave plate material makes a contribution.) Switching the pump-probe circular configuration to an anticircular one causes the ''antibound'' signals to disappear completely, as shown in the top trace of Fig. 3, where for comparison we include also the FWM spectra taken in the parallel-linear and co-circular-polarization configuration (bottom traces). For the anti-circular-polarization case, the FWM selection rules also imply vanishing $|B\rangle$ and $|X\rangle$ transitions; in Fig. 3 the weak residual contributions are most likely due to unavoidable (incoherent) luminescence signals reaching our detection system. For the positive time delays, we find that asymmetry of the excitonic resonance at $\tau=0$ weakens with increasing the time delay, and it eventually disappears after a time delay of also about 1.0 ps. Finally, we

note that further increase of the excitation density beyond the optimum value of 2×10^{11} cm^{-2} led to a reduction of the signal for amplitude of the antibound resonance (labeled $|A\rangle$) at a much faster rate than the corresponding decrease in $\chi^{(3)}$ for the bound molecular state.

In lieu of a detailed model for the explanation of our experimental results, we now make overview comments about the experimental results. The spectroscopic location of the ''resonance'' at $h\omega$=2.8175 eV and its very clear cocircular-polarization selection rule directly support the interpretation that an optical transition driven by continuum states of the excitonic molecule has been isolated in these experiments. The features appear only in the negative time-delay regime, underscoring the importance of interaction induced coherent polarizations. The theory of Schäfer *et al.*[2] appears to contain the key pieces of physics applicable to our case, namely, that the ''antibound'' contributions are a direct reflection from biexciton continuum contributions, generated as a consequence of dynamical interactions between 2D free excitons (though our system is only rather weakly 2D). In the context of bound biexcitons, it is shown in Ref. 2 how the FWM response can be dominated by the interaction between the two coherent excitonic polarizations (as opposed to coupling via optical fields), as a consequence of the interactions via the biexcitonic continuum scattering states. How this theory would predict the appearance of a rather well-defined spectral peak as the $|A\rangle$ transition suggests in Figs. 2 and 3 is not clear to us at this time, and we hope that the experimental results stimulate further theoretical work in this regard. We note that the coupling bound molecular state decays faster in negative time delay than in positive time delay[6] so that experimentally, a sub-ps temporal ''window of opportunity'' for the observation of the antibound states exists for $\tau<0$.

In terms of using the experimentally measured energy position of the peak of the $|A\rangle$ transition to roughly estimate an average energy for the antibound states, we turn to the recently developed model by Nair and Takagahara,[9] which has been successfully used to analyze excited exciton-pair states and nonlinear optical response in CuCl quantum dots in a weak confinement regime (where the dot's confining potential defines a radius $R\gg a_x$, the excitonic Bohr radius). In the present case we assume that the finite QW lateral potential variation provides (weak) localization in the QW layer plane so that an analogous quantum disk can be considered as a basis for applying the model in which exciton-exciton product states are used as the basis set. The in-plane localization of the four particles (at some unknown effective radius satisfying the condition $R\gg a_s$) allows one to separate out the center-of-mass motion. In our estimate of ΔE_a, we consider the thickness of the quantum disk to be fixed by the layer width of the QW whereas the in-plane localization radius is considered as an adjustable parameter. An expression for an antibound exciton state can be approximately written as

$$\Phi(r_1,r_2;r_a,r_b)=\phi(r_1,r_a)\phi(r_2,r_b)-\phi(r_1,r_b)\phi(r_2,r_a), \tag{1}$$

with the wave function $\phi(r_1,r_a)$ representing the exciton ground state with r_1 and r_2 (r_a and r_b) corresponding to the coordinates of the two electrons (holes). Denoting the total Hamiltonian for the four particles by H, the ''repulsion'' energy ΔE_a in Fig. 1(a) is calculated by

$$\Delta E_a=\langle\phi|H|\phi\rangle/\langle\phi|\phi\rangle-2E_x. \tag{2}$$

From the theory of Ref. 9, ΔE_a decreases with increasing lateral size of the quantum disk. We obtain $\Delta E_a\approx$3.5 meV for a lateral size of about 30 nm, a not unreasonable value for the ZnSe SQW material used in the experiments. In turn, this estimate is consistent with the excitation level of about 2×10^{11} cm^{-2}, which indicates that on the order of one or two excitons can fit into each quantum disk. Thus these theoretical considerations, although rough and requiring lateral exciton confinement that is only weak in the ZnSe QW, give some quantitative insight about the energy and spatial scale of the four-particle correlated states in question. At higher levels of excitation, these states are subject to increasing screening and annihilation by additional many-body effects, as observed in the experiment.

Finally, we note that we have not been able to observe a clear quantum-beat phenomenon involving the antibound state, in contrast with such observation of wave-function interference between the HH exciton and the bound state of the molecule in the ZnSe QW.[6] This is understandable in part due to the short-lived nature of the biexciton continuum states and the relatively small value of the energy ΔE_a, which corresponds approximately to the short time window where the effect is observable.[10] As already noted, from the spectroscopic experiment we obtain (Fig. 2) that $\Delta E_a\approx$3.5 meV, a value distinctly smaller than the bound exciton pair binding energy of 5 meV.

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