Excitonic molecules in ZnSe quantum wells

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Evidence for biexciton formation in ZnSe quantum wells is reported. The molecular binding energy is found to increase by one order of magnitude over the bulk value in narrow wells, in agreement with a recent calculation by Kleinman.

It is now well established that the forced confinement of free carriers within the same ultrathin layer of a semiconductor quantum well leads to an enhanced Coulomb attraction between electrons and holes and consequently to an increase in the exciton oscillator strength and its binding energy.[1] One expects a similar effect to occur for the biexciton, a molecular-like quasiparticle consisting of two electron-hole pairs bound together. A recent calculation of Kleinman[2] predicts that in the two-dimensional (2D) limit, the ratio of biexciton binding energy to exciton binding energy in a given material should exceed the corresponding three-dimensional value by a factor of 3–4. Given the fact that in the 2D limit the exciton binding itself is larger by a factor of 4, this represents altogether a possible increase of the molecular binding energy by more than an order of magnitude in a narrow quantum well. The presence of such stable excitonic molecules should be readily observable experimentally, especially by their contribution to radiative recombination spectra. To date, however, there is very scant evidence for biexciton formation in semiconductor quantum wells,[3] in sharp contrast to the situation of bulk materials, where evidence for biexciton formation has been reported in a large variety of crystals. This is probably due to the fact that most studies on quantum wells have concentrated so far on relatively small gap materials such as GaAs and related alloys, for which the binding of excitonic complexes is small in absolute terms and, therefore, not easily detectable.

In this paper we present experimental evidence for biexciton formation in ZnSe/(Zn,Mn)Se multiple quantum wells (MQW). Such ZnSe-based quantum wells represent a new class of artificial structures with wide band gaps which are now available with high material and structural quality.[4] We find that biexcitons are indeed strongly stabilized in these structures. As a consequence, biexciton recombination becomes the *predominant* emission feature in very narrow ZnSe quantum wells, even under conditions of weak excitation. Apart from fundamental interest, the understanding of recombination processes in ZnSe-based quantum wells is important, since these structures are promising materials for light-emitting diodes and injection lasers at blue wavelengths. For example, emission due to biexcitons may lead to very high optical gain,[5] in contrast to direct recombination of free excitons, for which no laser action is possible.

The structures used in this study were prepared by molecular beam epitaxy. A description of growth procedure and sample characterization is given in Ref. 4 and its references. Two MQW samples were the main focus in this work. The first structure, denoted as MQW 67, consisted of 67 periods of 67-Å thick ZnSe wells separated by 110-Å thick $Zn_{0.77}Mn_{0.23}Se$ barriers. The second structure MQW 24 had 76 periods of 24-Å thick ZnSe wells between 160-Å thick $Zn_{0.72}Mn_{0.28}Se$ barriers. The exciton Bohr diameter in bulk ZnSe is approximately 70 Å so that confinement effects were expected to play a major role, particularly for the sample MQW 24. The overall band-gap difference between the ZnSe well and $Zn_{0.72}Mn_{0.28}Se$ barrier is about 150 meV, a large fraction of which is thought to occur in the conduction band.[4] The main experimental results discussed here were derived from cw photoluminescence and its excitation spectra, obtained with a tunable blue dye laser (maximum power $P \sim 0.4$ W). Some luminescence spectra (not shown here) have also been recorded under conditions of strong excitation, using an amplified uv picosecond laser pulse ($\lambda = 350$ nm, maximum peak intensity $\sim 10^9$ W/cm^2).

A striking feature of the emission spectra near the superlattice band gap is their overall simplicity. The luminescence consists of the direct exciton recombination line (denoted by X) together with a line at lower energy (denoted by XX).[6] As shown in Fig. 1(a) in the MQW 67 sample, this second emission appears as a shoulder at longer wavelength, under conditions of weak excitation. In MQW 24, on the other hand, the second emission dominates the spectrum at low temperature even at the lowest excitations, as is clearly evident in the figure. Increasing the excitation intensity causes the line XX to grow significantly more rapidly than the direct exciton line for both samples as seen by comparing Figs. 1(a) and 1(b). The luminescence spectra obtained at highest levels of available cw excitation was readily reproduced by using amplified uv picosecond laser pulses; in this case, fur-

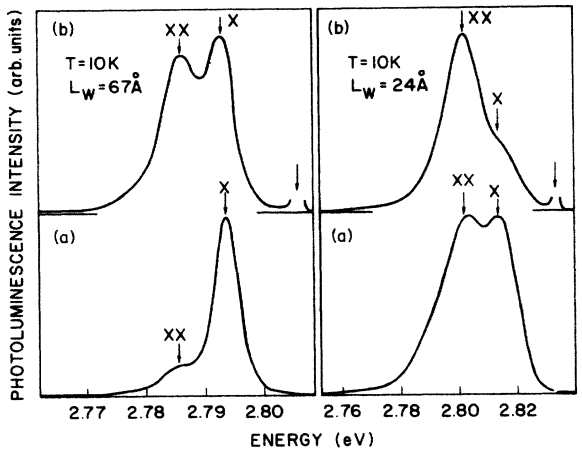

FIG. 1. Luminescence spectra of ZnSe quantum wells with well thickness $L_w = 67$ Å (left) and $L_w = 24$ Å (right), obtained at $T = 10$ K with cw excitation. The incident intensity is (a) 30 mW/cm^2 and (b) 100 W/cm^2. The arrows at the high-energy edge in spectra (b) indicate the excitation laser lines.

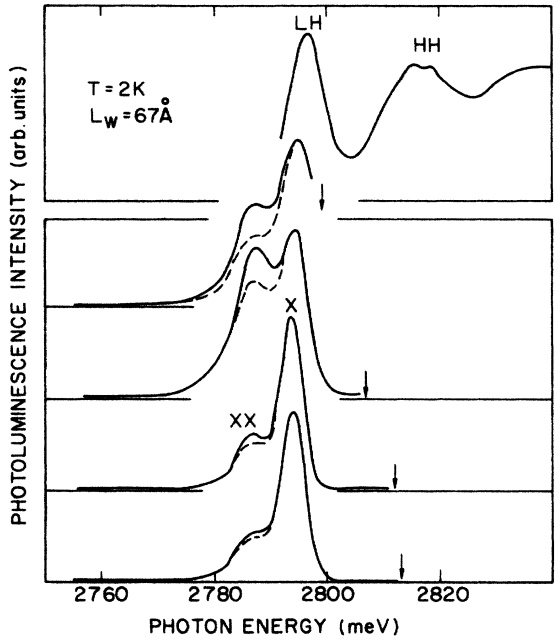

FIG. 2. Lower panel: Luminescence of ZnSe quantum well structure MQW 67, with $L_w = 67$ Å obtained with linearly polarized light (continuous curve) and circularly polarized light (dashed curve), under otherwise identical experimental conditions. Arrows indicate the incident photon energy for each curve. Sample temperature is 2 K. Emission curves are not to relative scale. Also, in the top luminescence curve, scattered laser light distorts the X line shape. Upper panel: The excitation spectrum of the sample, recorded at an emission photon energy $\hbar\omega = 2.787$ eV.

ther increase in excitation intensity showed that the amplitude of emission feature XX grows continuously without saturation up to the plasma limit. This aspect of our work will be discussed separately elsewhere. We now argue that line XX indicates in both cases the presence of biexcitons. In the elementary decay process, each biexciton gives rise to an exciton and a detected photon. This interpretation relies on the following summary analysis of our key results.

Kinetics. An alternate interpretation for XX could be an extrinsic exciton decay process, such as the recombination of an exciton bound to a donor.[6] However, an impurity related decay process is expected to show saturation at high excitations. On the other hand, the biexciton line should show the opposite behavior, namely an increase relative to free exciton line under increasing electron-hole pair injection. The observed trend with increasing excitation level is unambiguous and clearly points to an intrinsic recombination process such as the biexciton decay for the emission XX as already shown in Fig. 1. However, it is difficult to connect the observed exciton and biexciton line shapes quantitatively to kinetic rate equations because of presently insufficient knowledge about the details of these quasiparticles in the ZnSe quantum wells.

Polarization dependence. By using circularly polarized light instead of linearly polarized light from the excitation source, it is possible to impart a preferred spin orientation to the photocreated excitons.[7] In turn, this spin alignment of excitons should lead to a *reduction* of the biexciton emission relative to that from free excitons under otherwise identical conditions of excitation, since electrons must be in a relative spin-singlet state in order to bind into a molecule. Focusing on sample MQW 67, the top panel in Fig. 2 shows first for reference the luminescence excitation spectrum of the X emission line. The uniaxial component of the lattice mismatch strain ($\sim 0.6\%$) splits the exciton ground state in such a way that the "light-hole" exciton (LH) is at a lower energy. The lower panel in the figure compares luminescence spectra at $T = 2$ K obtained with linearly and circularly polarized incident light for sample MQW 67 (continuous and dashed curves, respectively) at different excitation photon energies. A very strong effect is observed for incident light tuned to the lowest (light-hole) exciton resonance as shown in Fig. 2 for the MQW 67 sample. At higher photon energies, spin-relaxation processes are more effective on the quasiparticles with larger initial energy and the polarization contrast is reduced. In the case of sample MQW 24, we have observed a similar behavior under circularly polarized excitation.

Giant two-photon absorption. It is well known that in bulk materials biexcitons can be created directly from the ground state by a two-photon absorption process with giant oscillator strength.[8,9] We have observed a similar effect in the ZnSe quantum well samples, by monitoring the excitation spectrum of line XX. A distinct, intensity-dependent peak in the excitation spectrum is observed for sample MQW 24 as illustrated in Fig. 3 for two different excitation intensities [3(a) and 3(b)]. Furthermore, this excitation peak displays the polarization selection rule expected for a paramolecular state as shown by comparison between linear and circular polarization in 3(c) and 3(d). Its position yields directly the total internal energy of the biexciton $E_{XX} = 2\hbar\omega = 5.62$ eV. In sample MQW

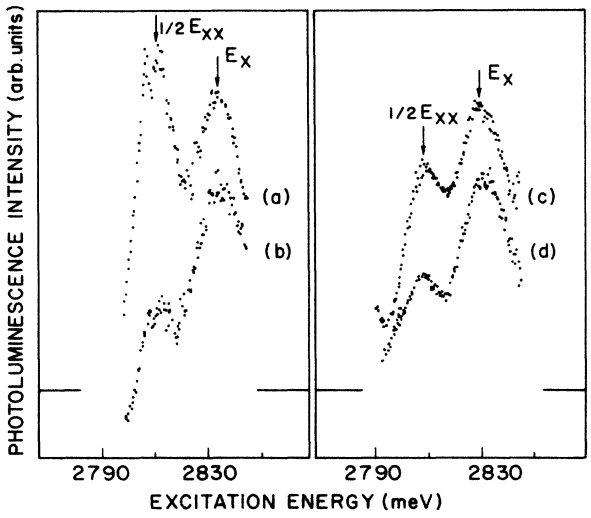

FIG. 3. Left: Excitation spectrum of MQW 24 recorded with high (a) and low (b) incident intensity ($I=250$ W/cm^2 and $I<30$ mW/cm^2). Right: Excitation spectrum recorded with $I\sim200$ W/cm^2 and linearly (c) or circularly (d) polarized incident light. In all cases the detected photon energy is 2.79 eV. Sample temperature is 2 K. Curves (a) and (c) have been displaced vertically for clarity.

67 an intensity dependence of the excitation spectrum of line *XX* is also observed when the incident light is below the exciton resonance. However, in this case we were not able to resolve a distinct two-photon excitation peak due to the proximity of the incident laser light to emission line *XX*.

Having established the biexciton nature of emission line *XX*, we now address the question of the biexciton binding energy B and its dependence upon well thickness. In principle, B can be determined either from luminescence or excitation data. In luminescence, the binding energy is found through the relation

$$\hbar\omega' = E_{XX}(k=0) - E_X = E_X - B \ ,$$

where $\hbar\omega'$ is the emitted photon energy at line *XX*, $E_{XX}(k=0)$ the total internal energy of the biexciton at rest, and E_X the internal energy of the exciton of lowest energy. A difficulty arises from our present lack of detailed understanding of the microscopic origin of the rather broad line shapes observed in the quantum wells. This prevents an accurate determination of $E_{XX}(k=0)$ and E_X, and consequently of B. For example, one factor contributing to the broadening as well as to spectral shifts in the exciton recombination energy is the unavoidable fluctuation of well thickness, which becomes increasingly effective in the case of narrower wells.[10] In turn such broadening may mask an underlying, more complex structure of exciton and biexciton levels.[11] We will assume in the following that $E_{XX}(k=0)$ is given by the peak of emission *XX* and E_X by the intensity-independent peak of the *excitation* spectrum.[12] This yields a value $B=11$ meV for MQW 67 and $B=33$ meV for MQW 24. In excitation spectroscopy, $B/2$ is given by the energy difference between the two-photon (biexciton) and one-photon (exciton) resonance. Again, taking the energy at the corresponding peaks in the spectra of Fig. 3, one obtains a value $B=40$ meV for MQW 24. For calibration we note that the exciton binding energy in bulk ZnSe is approximately 20 meV.

In view of this surprisingly large binding energy and because of the uncertainty in its determination mentioned before, we have performed an additional measurement to estimate B by monitoring the luminescence intensity as a function of temperature. A classical gas mixture of excitons and biexcitons in two dimensions in thermodynamical equilibrium should obey the following relation, obtained by equating the respective chemical potentials[13,14]:

$$n_{XX}/n_X^2 = CT^{-1}\exp(B/kT) \ ,$$

which is independent of excitation intensity. Here n_X and n_{XX} are the exciton and biexciton densities. From the temperature dependence of emission lines *X* and *XX* one obtains the following values: $B=13\pm3$ meV for MQW 67 and $B=35\pm10$ meV for MQW 24. The error corresponds to the uncertainty in the separation of the two lines. Again we find an indication of a substantial increase of the molecular binding energy over the bulk value $B_{3d}=3.5$ meV.[11] We note, however, that this trend is in agreement with the calculation of Kleinman[4] which, when applied to ZnSe, predicts a value $B_{2d}\sim50$ meV in the two-dimensional limit.

As a final comment, we wish to point out that not only the binding energy, but also the two-photon absorption cross section (which we did not measure so far) seems to benefit from the reduced dimensionality. Recall the clear appearance of the biexciton resonance in the excitation spectrum of Fig. 2, which was recorded with moderate input light intensity ($I_0<300$ W/cm^2) through a very small sample optical path $l\sim1$ μm. The phenomena may therefore have relevance in the search and design of materials with large optical nonlinearities.

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