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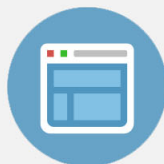
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Observation of coherent biexcitons in ZnO/ZnMgO multiple quantum wells at room temperature

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We have studied ZnO/ZnMgO multiple quantum wells by spectrally resolved transient four-wave mixing with both one- and two-color excitations. The presence of an extended signal at negative interpulse delays in the two-color experiment is attributed to the two-photon coherence resulting from the generation of biexcitons. This technique provides a means to observe a transient four-wave mixing from biexcitons in the absence of any other signal, and thereby provides the first clear evidence that biexcitons are present in narrow ZnO/ZnMgO quantum wells at room temperature. Dephasing times of the order of 100 fs for the biexcitons are measured. © 2006 American Institute of Physics. [DOI: 10.1063/1.2372747]

Wide band gap semiconductors such as the group III-nitrides and group II-oxides have attracted much attention in recent years because of their potential to fill the void in short wavelength optoelectronic devices. ZnO is one such material that has received particular attention recently. Compared to the group III-nitrides and other group II-oxides, ZnO has a large exciton binding energy (~ 60 meV),^{1,2} which should allow efficient excitonic lasing at room temperature. Furthermore, it is predicted, and has been shown in other semiconductor systems, that biexcitonic transitions play an important role in stimulated emission and can operate with an even lower threshold.³ The biexciton binding energy has been measured to be in the range of 12–16 meV in bulk ZnO,^{4,5} and in ZnO/ZnMgO quantum wells (QWs) it is expected to be enhanced due to quantum confinement. However, in competition to this, a strain induced electric field is present in these QWs (shown to be 0.9 MV/cm by Morhain *et al.*⁶), which reduces the exciton and biexciton binding energies. Nevertheless, when the wells are sufficiently narrow the confinement dominates,⁶ leading to observations of biexciton binding energies larger than 25 meV for QWs narrower than 2.5 nm.^{5,7} This is comparable to the thermal energy at 300 K, and opens the door to the possibility of biexciton lasing at room temperature with only minimal cooling required. Currently, however, there has been no experimental observation of biexcitonic emission from such samples at room temperature.

The simplest experimental means to observe biexcitons, and determine the binding energy, is to study the luminescence spectrum, where the biexciton peak appears at lower energy than the exciton and with amplitude that varies quadratically with excitation intensity. However, this becomes difficult in QWs at room temperature due to inhomogeneous

broadening and thermal broadening of the transitions. Spectrally resolved degenerate four-wave mixing (FWM) has also been used to observe emission from biexcitons in a background-free direction.^{8,9} However, the broadening again makes it difficult to resolve the biexciton peak, while the short dephasing time at room temperature makes it difficult to distinguish the biexciton signal from other many-body effects at short negative delays.

In this study, we use a combination of one- and two-color spectrally resolved transient FWM experiments to identify biexciton transitions in ZnO/ZnMgO quantum wells at room temperature. In a typical two-pulse degenerate FWM experiment, two laser pulses (pulse 1 and pulse 2) with the same wavelength and wave vectors \mathbf{k}_1 and \mathbf{k}_2 are incident on a thin sample, and the emission from the third-order polarization in the $2\mathbf{k}_2 - \mathbf{k}_1$ direction is detected. In this geometry, pulse 1 arrives first and establishes a polarization in the sample, then a photon from pulse 2 causes the generation of a population grating, from which a second photon from pulse 2 can diffract. Thus, a signal is observed only when pulse 1 arrives before pulse 2, hereafter referred to as positive delays. However, a signal can be generated at negative delays as a result of many-body effects, such as local-field effects, and excitation-induced dephasing.¹⁰ It is also possible to generate a signal at negative delays from biexcitons,¹¹ in which case the two photons from pulse 2 establish a two-photon coherence (i.e., the biexciton), from which a photon of pulse 1 can diffract, giving a signal in the $2\mathbf{k}_2 - \mathbf{k}_1$ direction that decays at a rate determined by the dephasing time of the biexciton. Indeed, this signal from a biexciton would be expected to exist almost entirely at negative delays.¹²

In the case of the two-color experiment, the “normal” signal would be expected to exist only where there is coherent transfer of the polarization from the state pumped by pulse 1 to the state probed by pulse 2. The signal from the two-photon coherence, however, can still exist where the two

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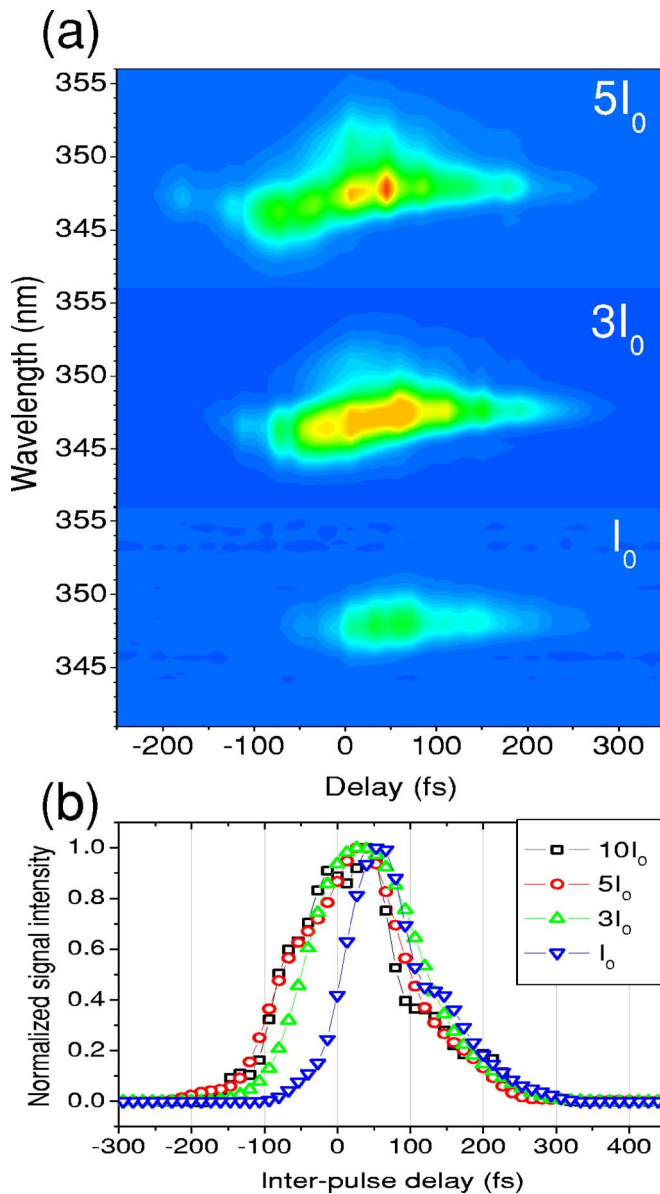


FIG. 1. (Color online) (a) Contour plots show the spectrally resolved transient FWM signal with 350 nm excitation from both pulses, for different excitation intensities as indicated. (b) The integrated data for four different intensities as labeled on the graph. At high intensity, the signal is spectrally broadened and persists at negative delays.

pulses are of a different color, since pulse 1 simply needs to diffract from the coherent biexciton. It is by the identification of this signal, using a two-color spectrally resolved FWM setup, that the presence of biexcitons at room temperature is identified.

Two optical parametric amplifiers pumped by a single Ti:sapphire regenerative amplifier with tunability below 350 nm and pulses 100 fs long were used to obtain the two pulses of different wavelengths, locked together in time. The pulses were linearly polarized, enabling the creation of biexcitons. The sample used in this experiment was a single crystal stack of 19 ZnO/Zn_{0.7}Mg_{0.3}O quantum wells, each 2 nm thick, grown on *a*-plane sapphire by molecular beam epitaxy as reported earlier.¹³ After growth, the sample was implanted with 80 keV O⁻ at a dose of 5×10^{14} cm⁻² at room temperature, followed by rapid thermal annealing at 800 °C in an Ar ambient for 60 s, as described by Coleman *et al.*¹⁴ The ion implantation and subsequent thermal anneal leads to inter-

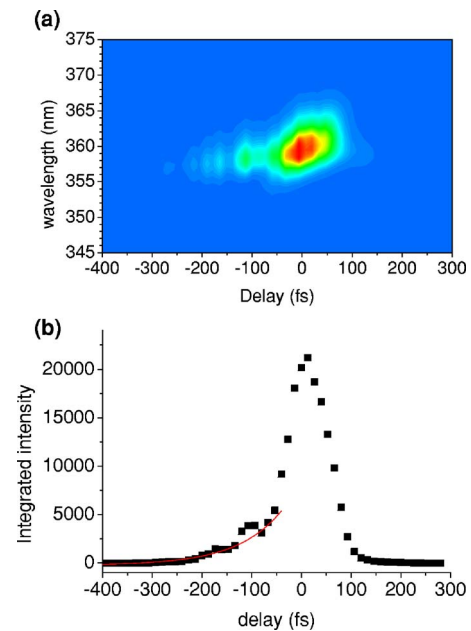


FIG. 2. (Color online) (a) Spectrally resolved and (b) integrated signals detected in the $2\mathbf{k}_2\text{-}\mathbf{k}_1$ direction from the transient FWM experiments, with wavelengths 340 and 350 nm for \mathbf{k}_1 and \mathbf{k}_2 , respectively. The line shown in (b) is an exponential fit to the data, which yields a dephasing time of the two-photon coherence of 100 ± 10 fs.

diffusion of the Zn and Mg in the barrier and well, thus allowing fine control of the quantum-well band gap. Both as-grown and intermixed samples were used in the current studies and coherent biexcitons were observed in as-grown as well as intermixed samples.

The photoluminescence spectrum of the sample discussed here shows a peak at 350 nm with a full width at half maximum of 20 nm. Figure 1 shows (a) the spectrally resolved and (b) integrated transient FWM data for different excitation intensities, with the wavelength of both pulses set to be resonant with the center of the quantum-well transition at 350 nm. It can be seen in the spectrally resolved data that as the intensity increases from $I_0 \sim 1$ mJ cm⁻² per pulse to $10I_0$ the signal spectrum is broadened. This is due to many-body effects, which become important at high excitation densities, and can include the presence of biexcitons. It is also apparent that as the delay between the pulses increases in the positive direction, the spectral width decreases, indicating that there is some signal from the sample after the excitation pulses have ceased temporally overlapping. The time evolution of the integrated signal provides further insight: For each of the four excitation intensities, the decay of the signal for positive delays remains the same; however, for negative delays, the decay time is very short for low excitation density, but increases with the intensity. This suggests that there is a significant signal at negative delays, beyond the temporal overlap of the two pulses, which is only present at high excitation density. The possible origins of this signal include excitation induced dephasing and the presence of biexcitons.

The origin of this signal is clarified by the results from the two-color experiments shown in Fig. 2. Here the wavelengths of pulse 1 and pulse 2 are 340 and 350 nm, respectively, and the signal in the $2\mathbf{k}_2\text{-}\mathbf{k}_1$ direction is again detected. The wavelength of the signal in this direction is given by $2\omega_2 - \omega_1$, which in this case corresponds to a signal at 360 nm as seen in Fig. 2(a). For a standard transient FWM

signal to be present in this configuration, there needs to be coherent transfer of polarization between the states excited by the 340 and 350 nm pulses. This is also true for any signal generated at negative delays due to local-field effects and excitation induced dephasing. Furthermore, the decay of such a signal at negative delays would be twice as fast as that at positive delays, as has been shown in theory¹⁵ and experiment.¹⁶ The experimental results show that there is only a rapid decay at positive delays, but an extended signal at negative delays, well beyond the time when the two pulses are temporally coincident. This is clear evidence that the extended signal arises from the generation of a two-photon coherence, most likely in the form of a biexciton. The intensity of the exciting pulses in the data shown was $5I_0$, and when it was reduced there ceased to be a signal, again replicating the behavior expected for biexcitons. The exponential fit of the decay of the signal is shown in Fig. 2(b) and gives a decoherence time for the two-photon coherence of 100 ± 10 fs. Given that these experiments were performed at room temperature, and phonons are expected to be the dominant cause of dephasing, this is a remarkable observation. Other sources of a two-photon coherence, such as an unbound exciton pair, would be expected to dephase even more rapidly, and within the laser pulse, due to increased interaction with the environment. The fact that a decoherence time is sufficiently long to be measured at all is a good indication that the two-photon coherence observed here is indeed a biexciton.^{17,18}

In conclusion, we have used a transient two-color four-wave mixing experiment to identify the presence of biexcitons in ZnO/ZnMgO quantum wells at room temperature. This technique allows the observation of the third-order emission from biexcitons in the absence of any other signal. Dephasing times of 90–110 fs for the two-photon coherence were obtained, giving great hope for the use of biexciton transitions in ZnO/ZnMgO quantum wells in blue-ultraviolet laser applications.

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