Coherent dynamics of excitons and biexcitons in intermixed ZnO/Zn$_{1-x}$Mg$_x$O quantum wells by ion implantation.

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Abstract—We have performed one and two colour, spectrally resolved four-wave mixing (FWM) experiments on a series of ZnO/Zn$_{1-x}$Mg$_x$O quantum wells with different oxygen ion implantation doses. The results show that at room temperature and with resonant excitation, excitonic coherences are maintained beyond the duration of the laser pulse. A transient signal observed at negative delays in the two-colour experiments is attributed to biexcitonic coherence. The use of the two colours allows the purely biexcitonic contribution to be resolved from any other many-body or excitonic contributions at negative delays; therefore the transient signal observed indicates the creation of biexcitons in the ZnO quantum well at room temperature. Coherence times as long as 480 fs at room temperature are found for both excitons and biexcitons and are shown to be independent of implantation dose.

Keywords - biexciton, coherence, ultrafast dynamics.

I. INTRODUCTION

Wide band-gap materials, such as the Group III nitrides, and II-VI semiconductors have attracted much interest recently as the push for devices that emit in the blue/UV region of the spectrum continues. With a band gap of 3.40 eV, large exciton binding energy of 60 meV [1, 2], and the availability of single crystal substrates, ZnO-based structures are ideal candidates. Post-growth tuning of the in-plane bandgap of quantum wells (QWs) is useful for optoelectronic device integration. One such technique is the use of ion implantation and subsequent rapid thermal annealing. This has been shown to lead to Zn/Mg intermixing, thus presenting a means to finely tune the bandgap of ZnO/Zn$_{1-x}$Mg$_x$O quantum wells [1]. Ion implantation creates defects which encourage the interdiffusion of Mg and Zn across the barrier and quantum well interfaces during the thermal annealing process. The thermal treatment process also anneals the defects introduced by implantation and our initial results showed good recovery of the cathodoluminescence signal after annealing. However, a thorough investigation into the effect of the ion implantation and subsequent thermal anneal on the quality of the quantum well structures and interfaces has not been studied previously. The spectrally-resolved four-wave mixing (FWM) experiments presented here, studying the coherent dynamics of these systems, provide an excellent means to examine the permanent changes to the QWs induced by the ion implantation.

Another advantage of ZnO is that the biexciton binding energy in ZnO-based quantum wells has been shown to be greater than the thermal energy at room temperature [3-7]. This provides an opportunity for room temperature lasing in the blue/UV region of the spectrum using biexcitons, which are expected to have a lower threshold than excitons [8]. Currently, however, there has been no experimental observation of biexcitonic emission from such samples at room temperature. Usual means of observing biexciton effects include photoluminescence, spectrally resolved FWM [9, 10], and quantum beat spectroscopy. All of these techniques rely on the ability to spectrally resolve the biexciton peak from the single exciton peak and, at room temperature, this is difficult due to thermal and inhomogeneous broadening. Using the two-colour spectrally-resolved FWM setup described here, we are able to separate in time the coherent biexciton signal from any other signal.

II. EXPERIMENT

The samples used in this experiment were modified from a single crystal stack of 19 ZnO/Zn$_{0.7}$Mg$_{0.3}$O multi quantum well structure, with 2 nm QWs and 5.5 nm barrier layers, grown on $c$-plane sapphire by molecular beam epitaxy as described elsewhere [11]. After growth, the sample was divided and implanted with 80 keV oxygen ions at a dose ranging from 5×10$^{14}$ - 1×10$^{16}$ cm$^{-2}$ at room temperature, followed by rapid thermal annealing at 800º C in an Ar ambient for 60 s, as described by Coleman et al. [12]. The ion implantation and subsequent thermal anneal leads to interdiffusion of the Zn and Mg in the barrier and well, thus allowing fine control of the quantum-well bandgap.
The FWM experiments were performed with two pulses labelled $k_1$ and $k_2$, representing their wavevectors, coming from separate optical parametric amplifiers pumped by a single Ti:sapphire regenerative amplifier. The pulses are tunable from below 350 nm to longer than 1 micron, and are about 100 fs long. Two CCDs and spectrometers were used to detect and spectrally resolve the signals emitted in both phase-matched directions, $k_3 = 2k_2 - k_1$ and $k_4 = 2k_1 - k_2$.

III. RESULTS AND DISCUSSION

The photoluminescence (PL) spectra of the samples discussed here are shown in Fig 1, where it can be seen that the ion implantation has the effect of blue-shifting the peaks. It is also noticeable that the samples with ion-implantation have a significant tail at longer wavelength. This is due to the fact that the extent of implantation is not constant through the sample, and the deeper QWs receive a much lower dose, and so are not as blue-shifted [12].

![Figure 1. Photoluminescence spectra for the three ZnO/ZnMgO QW samples: with no implantation, an implantation dose of $5 \times 10^{14}$ cm$^{-2}$ and an implantation dose of $5 \times 10^{15}$ cm$^{-2}$.](image1)

Figure 2 shows the spectrally resolved and integrated signals from the two-pulse degenerate FWM experiments for the samples without implantation, and with implantation doses $5 \times 10^{14}$ and $5 \times 10^{15}$ cm$^{-2}$. The wavelength of the pulses was selected to be resonant with the peak observed in the corresponding PL spectrum. The data shown is from the $k_3 = 2k_2 - k_1$ direction, and is identical to that in the $k_4$ direction apart from a reversal in the time delay axis. In the data shown, the delay is positive when $k_1$ arrives before $k_2$, and hence an extended signal at positive delays indicates the presence of some coherence remaining in the system beyond the overlap of the laser pulses. The asymmetry in the spectrally resolved and integrated signals for each of the samples in Figure 2, seen as a tail towards positive delays, is a clear indication of such coherence. The decay of this signal occurs at a characteristic rate $4/T_2$, where $T_2$ is the decoherence time of the excitons, assuming the transition is inhomogeneously broadened, which from the spectra appears to be a reasonable assumption. By fitting a single exponential decay to each of the spectrally integrated curves, decoherence times of $290 \pm 20$ fs were found for each of the samples. Room temperature dephasing times for III-V semiconductor QWs are typically in the range 200-250 fs [13], of the same order but slightly shorter than the values obtained in these ZnO QWs. The invariance of decoherence time with implantation dose suggests that the dominant dephasing mechanism in these samples is unaltered by the impurities in the lattice, at which excited charges can be ion implantation. It also suggests that the number of localised, is not altered by the ion implantation, as this would be expected to increase $T_2$. This thereby suggests that oxygen ion implantation and subsequent thermal annealing leaves minimal residual defects and is a promising technique to alter the bandgap of ZnO/ZnMgO quantum wells, and opens the door to further investigation.

![Figure 2. (a) Contour plots showing the spectrally resolved transient FWM signal for (a) the sample with no implantation with 370 nm excitation from both pulses, (b) the sample with implantation dose $5 \times 10^{14}$ cm$^{-2}$ with 360 nm excitation from both pulses and (c) the sample with implantation dose $5 \times 10^{15}$ cm$^{-2}$ with 330 nm excitation from both pulses. The integrated data for the three samples is shown in (d), from which a dephasing time of $280 \pm 40$ fs is obtained.](image2)
magnitude, the magnitude of the signal at negative delays gradually increases, and the spectrum broadens, as described elsewhere [14]. These effects are due to many-body effects [15, 16], which become important at high excitation intensities and include local-field effects, excitation-induced dephasing [17], and biexcitons [18]. In the case of biexcitons, the signal is generated from a two-photon coherence (i.e., a coherent biexciton), from which the third photon can diffract, giving a signal in the phase-matched directions that decays at a rate determined by the dephasing time of the biexciton [19]. In the one-colour FWM experiments, it is not possible to determine the origin of this signal, and indeed all of the many-body effects mentioned may be contributing.

In order to further elucidate the origin of this signal at negative delays, two-colour FWM data was collected for each sample. In these experiments, a signal from single excited charge carriers or excitons would be expected to exist only where there is coherent transfer of the polarization from the state pumped by \( \mathbf{k}_1 \) to the state probed by \( \mathbf{k}_2 \). However, a signal from a two-photon coherence can still exist where the two pulses are of a different colour without any transfer of coherence between states. Additionally, in contrast to the other many-body effects mentioned, biexcitons can give a signal at negative delays with no corresponding signal at positive delays [19]. Hence, the appearance of a signal only at negative delays indicates the presence of coherent biexcitons. In general, signals at positive delays from biexcitons are observed [19, 20]. However, in the two-colour experiment, because the electric fields of the two pulses are not oscillating at the same frequency, and hence the phase relationship between them is not constant, the creation of a coherent biexciton by one photon from each pulse is not probable, and so no signal is expected at positive delays.

Figure 3 shows the spectrally resolved and integrated data from the two-colour FWM experiments, with \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \) set to 360 nm and 370 nm respectively, for each of the samples studied. The signal detected and shown here is again the one in the \( \mathbf{k}_1 \) direction, and the frequency is given by \( 2\omega_2-\omega_1 \), where \( \omega_2 \) and \( \omega_1 \) are the frequencies of \( \mathbf{k}_2 \) and \( \mathbf{k}_1 \) respectively, and in this case corresponds to a signal around 380 nm. The data in Figure 3 show this signal at ~380 nm with an extended signal to negative delays. To check the validity of the signal, and ensure it was not due to asymmetry in the laser lines, spectra were taken of both laser pulses, which confirmed their symmetry. Additionally, the wavelengths of the two lasers were swapped, and still the extended signal at negative delays only was observed. In Fig 3(b), and to a lesser extent in Fig 3(a) and (c), two signal peaks spectrally separated by about 28 meV can be seen at negative delays. This energy value is very close to the biexciton binding energy expected in these systems, and it is likely that the two peaks are due to the presence of biexcitons. These results thereby strongly suggest the presence of coherent biexcitons in the ZnO QWs at room temperature.

The integrated data shown in Fig 3(d) show that the decay of this signal is very similar for each of the samples studied and apparently independent of ion implantation dose. Fits of the data with an exponential decay yield decay times of around 120 fs. In the case of a two-photon coherence, there is no rephasing to generate a photon echo, and so this decay must be related to the dephasing time of the biexciton as \( 2/T_2 \), thereby giving \( T_2 \) for the biexcitons as 240 fs. This is within experimental uncertainty of the values found above for the decoherence times of excitons under similar conditions, and so indicates that the dominant dephasing mechanism is the same, most likely phonon scattering. Other potential 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. Indeed, 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 [21, 22].
Several different wavelength combinations of \( k_1 \) and \( k_2 \) in the range 340-370 nm were used for each of the samples studied. Whilst there were differences observed for the different wavelengths, an extended decay at negative delays was observed to some extent in all cases. In each case, the differences in the decays of the signals for the different samples were quite small and difficult to differentiate. This has prevented a clear comparison of the effect of ion implantation on the biexciton decoherence time. However, these initial results suggest that the ion implantation has little effect on the dephasing and localisation mechanisms in the ZnO/ZnMgO QWs studied here.

IV. CONCLUSIONS

In conclusion, decoherence times of excitons in ZnO/ZnMgO QWs of \( 280 \pm 20 \) fs at room temperature have been obtained, and found to be independent of ion implantation. Additionally, we have used a transient two-colour 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, and again little difference between samples with different ion implantation doses was observed. These observations suggest that the implantation of low energy oxygen ions followed by a rapid thermal anneal leads to few permanent defects in the QW structures. This is an important development, giving further significance to this means of engineering the QW bandgap post-growth. The additional observation of coherent biexcitons at room temperature gives great hope for the possible future use of the biexciton transition in ZnO/ZnMgO quantum wells in blue-ultraviolet laser applications.

ACKNOWLEDGMENTS

We gratefully acknowledge The Australian Research Council for financial support, and Swinburne University of Technology for Strategic Initiative funding.

REFERENCES