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Ultrafast dynamics in ZnO/ZnMgO multiple quantum wells

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Abstract
We have investigated carrier relaxation and exciton recombination dynamics in ZnO/ZnMgO multiple quantum wells using femtosecond pump–probe techniques at room temperature. For a probe energy above the band gap, the hot carriers exhibit an effective relaxation by longitudinal optical phonon scattering with a cooling time of 700–850 fs. By detecting the emission near the band-gap, a longer decay time of a few picoseconds was observed which is attributed to acoustic phonon scattering. As the probe energy is decreased further, the decay time continues to increase due to the transitions of exciton recombination or localized carrier recombination.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently ZnO has attracted much attention as a potential material in short-wavelength optoelectronics applications because of its large fundamental band gap of ∼3.3 eV at room temperature [1]. ZnO has some additional advantages compared to other large band-gap materials; for example, its large exciton binding energy (about 60 meV) is about three times the binding energies of ZnSe and GaN [2, 3], which allows a stable exciton distribution and achieves efficient excitonic emission at room temperature. Furthermore, due to the enhancement of the binding energy and the reduction of the exciton–phonon coupling in quantum confined structures, the excitons in ZnO-based quantum well heterostructures exhibit even greater stability compared to ZnO bulk materials [4] and thus excitons are expected to play an important role in ZnO-based quantum wells.

Optical probing of ultrafast dynamics in semiconductor nanostructures has yielded many new insights for the understanding of detailed ultrafast relaxation and recombination processes. Extensive time-resolved optical investigations on carrier relaxation processes have been conducted in ZnO thin films. Upon high excitation, Yamamoto *et al* observed hot carrier cooling on the order of less than 1 ps in ZnO epitaxial thin films [5]; Sun *et al* recently reported the observation of an extremely fast thermalization time on the order of 200 fs at low excitation and a prolonged carrier cooling process at high excitation in ZnO epitaxial thin films [6]. Using an optical Kerr gate technique, Takeda *et al* studied ultrafast time-resolved photoluminescence (PL) in ZnO epitaxial thin films [7]. Ultrafast dynamics were also studied in ZnO nanostructures. Johnson *et al* reported the observation of a 400–1000 fs fast transient in ZnO nanowires and nanoribbons [8]; time-resolved photoluminescence experiments were performed at the near-band-gap region in ZnO/ZnMgO quantum wells to elucidate the basic properties [9, 10]. However, to the best of our knowledge, to date, femtosecond carrier dynamics in ZnO/ZnMgO multiple quantum wells (MQWs) has not been reported. A clarification of hot carrier cooling and exciton recombination is important for ZnO-based quantum wells, not only for

understanding their optical properties but also for potential device applications.

In this study we investigate ultrafast dynamics of hot carrier relaxation in ZnO/ZnMgO multiple quantum wells using femtosecond pump–probe techniques at room temperature. For a probe energy above the band edge, an effective carrier cooling process by longitudinal optical (LO) phonon scattering is probed with a subpicosecond cooling time. For a probe energy near the band gap, the exciton-acoustic phonon scattering results in a relaxation time of a few picoseconds. With decreasing probe energy the decay time continues to increase.

2. Experimental sample and technique

The sample used in this study was a single-crystal stack of 19 ZnO/$Zn_{0.7}Mg_{0.3}O$ multiple quantum wells grown on *a*-plane sapphire by molecular beam epitaxy [11]. This sample consists of a 10 nm thick ZnO buffer grown at low temperature (250 °C), followed by a 500 nm thick ZnO layer grown at 500 °C. Then 19 layers of ZnO/$Zn_{0.7}Mg_{0.3}O$ quantum wells (thickness 2 nm)/barriers (thickness 5.5 nm) were grown on top of the ZnO buffers. The multiple quantum wells were capped by a 50 nm layer of $Zn_{0.7}Mg_{0.3}O$.

The time-resolved experiments were performed using a transmission pump–probe technique with two independently tunable optical parametric amplifiers pumped by a Ti:sapphire regenerative amplifier. The pump and probe beams are focused by a 20 cm focal length lens on to the same spot (diameter 100 μm) on the surface of the sample with a small angle between the pump and probe beams. The optical parametric amplifier has an ultra-short pulse duration of 100 fs with a repetition rate of 1 kHz for both pump and probe. The pump pulse is tuned and fixed to 3.64 eV, which corresponds to above band edge absorption of ZnO quantum wells but is significantly lower than the absorption energy of the $Zn_{0.7}Mg_{0.3}O$ barriers. Thus electron and hole pairs are generated in the excited states of the quantum wells by the pump pulses. The excitation density of the pump is about 1 mJ cm^{-2}/pulse and the corresponding excitation density of electron–hole pairs can be estimated as 1×10^{20} cm^{-3} from the penetration depth and the spot size of the excitation pulses at the sample. This excitation density is larger than the critical Mott transition density of ZnO [12] and thus electron–hole plasma may be the important form of carriers in the band-gap region [12]. In the pump–probe experiment the ZnO/ZnMgO MQW sample is excited and a variation of optical properties is induced by the pump pulse. The probe beam is suitably delayed with respect to the pump pulse by introducing an optical delay in its path, and the minimum step size corresponds to a time of 10 fs. The transmission variation of the probe was detected by a charge-coupled device (CCD) to investigate the variation in the sample induced by the pump. In all probe wavelengths the transmission signal is very weak prior to the pump pulse and significantly increases after the pump.

The photoluminescence experiment is performed using excitation by the third harmonic of the fundamental pulses (wavelength 800 nm) from the Ti:sapphire regenerative amplifier, with a wavelength of 266 nm, a pulse duration of 100 fs and a 1 kHz repetition rate. The retro-reflected PL is detected by an UV–visible response photomultiplier tube at the output slit of a 0.25 m monochromator.

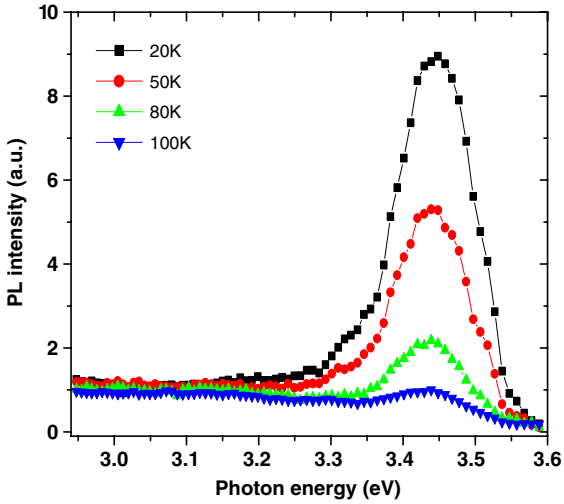

Figure 1. Photoluminescence spectra of ZnO/ZnMgO multiple quantum wells at low temperatures excited by 266 nm laser.

3. Experimental results and discussion

Figure 1 shows the photoluminescence spectra of ZnO/ZnMgO MQWs at low temperatures excited by a 266 nm laser. A significant luminescence band from the quantum wells is observed with an emission peak at 3.45 eV and a full width at half maximum (FWHM) of 150 meV. This PL band is blue shifted with respect to bulk ZnO because of the strong quantum confinement and relatively weak quantum-confined Stark effect [13], similar to previous observations in ZnO/ZnMgO QWs [14, 15].

The band-edge photoluminescence has been studied extensively in ZnO bulk, films, quantum wells and other nanostructures, and the origin of the PL spectra in the near-band-gap region has been proposed [1, 16, 17]. At low temperatures, the PL spectra near the band gap consists of transitions of free and bound excitons, followed by their longitudinal optical phonon replica on the low-energy side as a shoulder [6]. In our PL experiment, the emission from the ZnMgO barriers is too weak to be observed; however, it was observed in cathodoluminescence experiments at about 3.91 eV [18]. This suggests an effective carrier capture from the barrier into the quantum wells.

With increasing temperature, the intensity of the PL decreases significantly due to non-radiative centre activation. Above 200 K the PL of the quantum wells is almost washed out by the band-edge emission of the ZnO. The near-band-edge PL band becomes broad at room temperature due to strong inhomogeneous broadening and thermal broadening. The band-edge PL of ZnO multiple quantum wells was studied by Makino and colleagues, who found that the room-temperature photoluminescence spectrum is dominated by exciton recombination [19]. The weak PL spectrum due to thermal annihilation suggests that non-radiative recombination, rather than radiative recombination, is dominant at room temperature. It is difficult to identify the

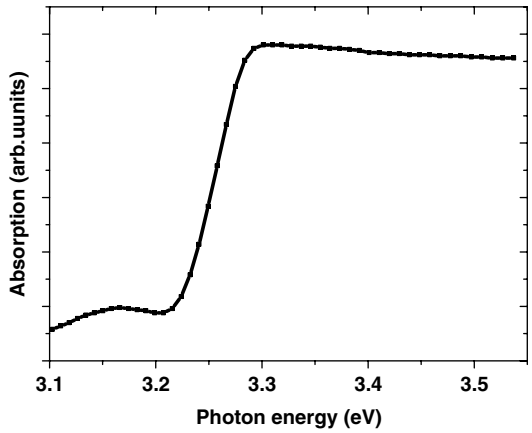

Figure 2. Room-temperature absorption spectrum of ZnO/ZnMgO multiple quantum wells. The absorption of the quantum wells is masked by that of the ZnO layer under the quantum wells due to the much thicker ZnO layer.

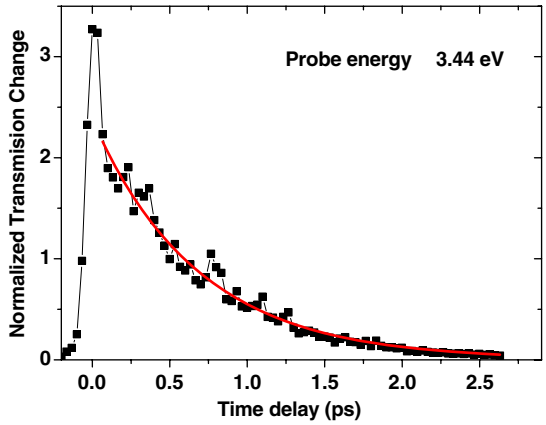

Figure 3. Time evolution of transmission probed at 3.44 eV and the corresponding single exponential function fit. A decay time of 830 ± 20 fs is deduced.

detailed wavelength of the transitions from the PL experiments due to inhomogeneous broadening and thermal broadening, and the low quantum efficiency at room temperature. We can estimate the band gap to be around 3.4 eV, based on the PL peak of 3.45 eV at low temperature in our experiment and estimates for the Stark shift and band-gap shift in going from 20 to 300 K from previous measurements in ZnO/ZnMgO quantum wells with a similar well width and composition [10]. Makino and colleagues also acquired a similar room-temperature band gap from $ZnO/Zn_{0.73}Mg_{0.27}O$ multiple quantum wells with a width of 2.35 nm [19].

We measure the absorption spectrum of the sample as shown in figure 2. However, this does not show the absorption of the quantum wells, because the measured beam passes through 38 nm of quantum well layers as well as 500 nm thick of ZnO layer, and the thickness of ZnO layer is much larger than that of the quantum wells. Therefore the absorption of the quantum wells is masked by that of the ZnO layer. The band gap of 3.3 eV is consistent to the other measurements in ZnO bulk materials at room temperature [1].

In the transmission pump–probe experiment, the dynamics can be determined by coherent and incoherent responses of the system. In general, the coherent response in semiconductors is extremely fast and thus one needs to use semiconductor Bloch equations to calculate the third-order nonlinear polarization. The incoherent effects can be divided qualitatively into two general classes [20]. The first class includes many-body effects, such as band-gap renormalization, which result in a change of the energy band structure, a change of the exciton binding energy, broadening of the energy levels or a change in the various matrix elements. This class generally takes place in an extremely short time for a ZnO system [6]. In our experiment the signal corresponding to this class may coincide with the coherence spike. The second class includes occupation effects, such as the changes in the optical properties or transition rates brought about by the non-equilibrium occupation of certain states. When the probe pulse is incident at a given photon energy, absorption, spontaneous emission and stimulated emission can all occur simultaneously. The absorption at a given photon energy is reduced if the final state is partially occupied. At the same time, stimulated emission may make a large contribution to the detected signal for a high-intensity pump. In this case, the pump pulse generates a large number of photoexcited carriers in a higher state and these photoexcited carriers relax quickly into the lower levels. Stimulated emission is induced by the probe pulse if there is a large number of carriers in the corresponding level. Spontaneous emission will make only a minor contribution, because it should emit in a large solid angle and the detection is only in a very small solid angle. Therefore the variation of the probe transmission signal reflects the variation of population occupation in the given detection level.

For the 3.64 eV pump excitation, electron–hole pairs are generated in the excited state of the quantum wells and they can instantaneously convert partially into excitons with an amount of excess energy. Immediately after the pump pulse, a very short coherence spike appears within tens of femtoseconds [21]. The hot carriers and excitons generated by the pump pulses can rapidly relax down to quasi-thermal equilibrium states, mainly by LO phonon scattering, resulting in a quasi-equilibrium distribution of thermalized carriers [6, 7]. At room temperature this process can be very fast because of efficient carrier energy cooling through LO phonon scattering in the two-dimension quantum wells. In the near-band-gap region acoustic phonon scattering can result in a minor and relatively slow relaxation due to a weak coupling strength and small phonon energy. The subsequent processes consist of localization at potential fluctuations, scattering with electrons or other excitons, and eventually recombination radiatively or non-radiatively on a timescale of tens of picoseconds [22].

In the above-band-edge region, the time evolution of the transmission probe is very fast, as shown in figure 3 for the probe energy of 3.44 eV, while in the the below-band-edge region a significantly slower evolution is observed and the time evolution at a probe energy of 3.30 eV is shown in figure 4, in which the timescale is ten time larger than that in figure 3 for the above-band-edge region. These evolutions can be fitted using a single exponential function and the corresponding decay times are deduced, as shown in figure 5 for various probe photon energies.

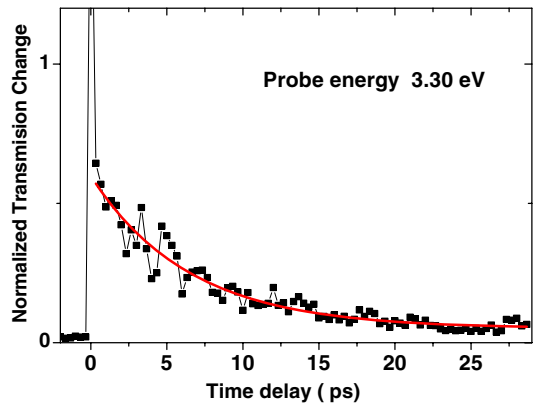

Figure 4. Time evolution of transmission probed at 3.30 eV and the corresponding single exponential function fit. A decay time of 6.4 ± 0.5 ps is deduced.

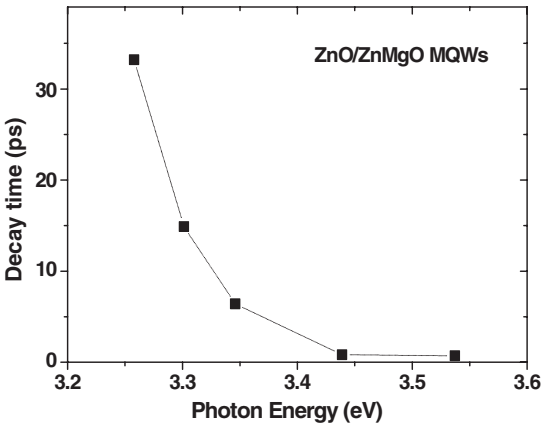

Figure 5. Decay times as a function of the probe energy in ZnO/ZnMgO multiple quantum wells.

For a probe energy above the band edge, e.g. 3.54 and 3.44 eV, immediately after the pump pulse a very short peak is observed as a coherence spike. Then a population decay process follows, e.g. carrier relaxation and exciton recombination. At probe energies of 3.54 and 3.44 eV, decay times of 710 ± 20 fs and 830 ± 20 fs are deduced from the transmission evolution with a single exponential function fit. These probe energies correspond to the above-band-gap region and thus the dominant decay mechanisms should be carrier and exciton relaxation to the quasi-thermal equilibrium states. In these ZnO quantum wells with a high LO phonon energy of 72 meV and strong carrier or exciton–phonon coupling, very effective LO phonon-assisted relaxation is achieved [6] and thus a very short cooling time of 700–850 fs is attributed to the LO phonon-assisted relaxation, which is similar to previous observations in ZnO films [6, 8]. At higher probe energy, a slightly longer cooling time is observed, which is likely due to scattering with the fewer LO phonons.

For a probe energy just below the band gap, e.g. 3.35 eV, the carriers and excitons can relax to the lower levels and exciton recombination is not the effective relaxation approach due to the relatively long lifetime of excitons. The dominant relaxation mechanism should be exciton-acoustic phonon scattering, because LO-phonon scattering is not possible due to the large LO-phonon energy of 72 meV in ZnO. A relatively long cooling time at this probe energy is observed with 6.4 ± 0.5 ps due to a much smaller coupling strength for acoustic phonons compared to that of LO phonons [7].

With decreasing probe energy, e.g. 3.30 and 3.26 eV, which is below the band gap of the quantum wells, a lower absorption is expected. On the other hand, this detection energy is close to the band gap of the ZnO bulk layer. Compared to the high detection energy, the probe beam experiences a different absorption. In this region the main transitions include the carrier recombination from the localized states of quantum wells and exciton or carrier recombination from the ZnO layer. At the lower probe energy, an increased decay time is observed due to non-radiative transfer processes to the tail states [10].

4. Summary

We have investigated the carrier and exciton dynamics of ZnO/ZnMgO multiple quantum wells using femtosecond resolution pump–probe experiments. In the above-band-gap region, strong LO-phonon scattering results in effective carrier relaxation with a cooling time of 700–850 fs. In the near-band-gap region, a relatively long cooling time of 6 ps is observed due to a weak carrier-acoustic or exciton-acoustic phonon coupling strength. As the probe energy is decreased to the below-band-gap region, the decay time continues to increase due to the transitions of exciton and localized carrier recombination from quantum wells and ZnO layer.

Acknowledgments

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