Femtosecond Dynamics of Resonantly Excited Room-Temperature Excitons in II-VI CdZnTe/ZnTe Quantum Wells

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The femtosecond pump and probe technique, with 14-fs probe pulses, was used to measure exciton dynamics utilizing the unique characteristics of II-VI CdZnTe/ZnTe quantum wells, at room temperature. We have found that the bleaching effect of "cold" neutral excitons on excitons is stronger than that of the same density of "cool" uncorrelated charged electron-hole pairs, in disagreement with predictions. We find strong evidence, however, that long-range Coulomb screening is negligible in quasi-2D quantum wells. Additionally, we have measured a very fast exciton ionization time of 110 fs.

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In semiconductor multiple quantum wells (MQWs), the quantum confinement of carriers enhances excitonic behavior, resulting in well-resolved excitonic absorption peaks even at room temperature [1]. With increasing carrier densities, the excitons (strongly correlated electron-hole pairs with Coulomb interaction) are screened and eventually lose their oscillator strengths [2]. As a result, the excitonic absorption will be greatly reduced or bleached. One interesting question is how strongly can excitons, which are electrically neutral but consist of electrons and holes, self-screen the exciton. In bulk GaAs Fehrenbach *et al.* [3] observed that the screening of excitons by excitons is very weak, compared to the screening of excitons by free carriers. Recently, Knox *et al.* [4] directly compared the absorption-bleaching strengths of excitons and free carriers from femtosecond time-resolved measurements. In those measurements, excitons were resonantly created and ionized into the same number of free electron-hole (*e-h*) pairs within about 300 fs, by longitudinal optic (LO) phonon scattering, at room temperature. They found that the bleaching effect of excitons on excitons was stronger than that of the same density of "warm" free carriers in GaAs MQWs. This behavior is qualitatively well explained by the Pauli exclusion principle based theory of Schmitt-Rink, Chemla, and Miller [5]. However, the studies of absorption bleaching in III-V MQWs are limited to warm or "hot" free *e-h* pairs ($kT/E_X^b \approx 3$–10, where T is the carrier temperature), since the LO phonon energy ($h\nu_{LO} \approx 30$–40 meV) is much larger than the exciton binding energy ($E_X^b \approx 1$–8 meV). As a result, ionized *e-h* pairs in III-V MQWs have, initially, very large excess energies [$\Delta E \geq 25$ meV $\approx$ (thermal energy) $\equiv kT_L$] and remain hot [4,6].

In this Letter, we report the first direct measurement of the relative bleaching strength of excitonic absorption by "cool" free *e-h* pairs ($kT/E_X^b \approx 1$) and cold excitons. For this study, wide-gap II-VI CdZnTe/ZnTe MQWs, which show well-defined room-temperature excitonic absorption peaks [7], are uniquely qualified, since E_X^b, $h\nu_{LO}$, and kT_L are all comparable. For the femtosecond pump and probe measurement, broad band 14-fs probe pulses are employed to elucidate the dynamical response, induced by 80-fs pump pulses. Surprisingly, we have found that the bleaching effect of cold neutral excitons on excitons is stronger than that of the same density of cool uncorrelated charged *e-h* pairs, in disagreement with the prediction of Ref. [5]. This result, however, strongly confirms that long-range Coulomb screening is negligible in quasi-2D MQWs. Additionally, we have measured a very fast exciton ionization time, 110 fs, which agrees well with estimates from the homogeneous linewidth broadening. This supports the fact that the thermal broadening is mainly due to the ionization of excitons through LO phonon scattering. The 110-fs ionization time is significantly faster than that of III-V quantum wells (≈ 300 fs) [4,6], reflecting the stronger exciton–LO-phonon interaction in this wide-gap II-VI MQW system [7].

The sample used in this study consists of fifteen periods of 50-Å-thick $Cd_{0.43}Zn_{0.57}Te$/ZnTe wells, alternated with 95-Å-thick ZnTe barriers. The MQW is grown by molecular-beam epitaxy on a (001)-oriented semi-insulating GaAs substrate, followed by a ZnTe epilayer 1.2 μm thick and a $Cd_{0.12}Zn_{0.88}Te$ buffer layer 2 μm thick. The MQW side was epoxied down on a sapphire disk and the GaAs substrate was then selectively etched. To reduce Fabry-Pérot effects, antireflection coatings of SiO and Al_2O_3 were deposited on the MQW to epoxy interface and the epilayer to air interface, respectively. The absorption spectrum in the vicinity of the exciton peak, taken with a lamp, at room temperature, is shown in Fig. 1. The well-defined $n=1$ heavy-hole exciton peak is centered at 619 nm and the observed linewidth (full width at half maximum) is about 6.5 nm (21 meV). The spectra of the 80-fs pump pulse and the broad band probe pulse are also shown. The absorption coefficient at the peak of the excitonic resonance is 1.8×10^4 cm^{-1}, with respect to the total thickness of the wells plus the barriers.

The femtosecond dynamics were studied by the pump and probe technique [8]. The ultrashort pulse source consists of a colliding-pulse mode-locked dye laser am-

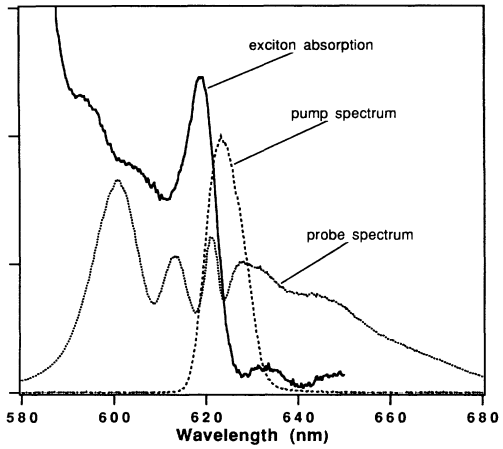

FIG. 1. Room-temperature absorption spectrum of the CdZnTe/ZnTe quantum well sample (smooth curve) and the spectra of the 80-fs pump pulse and 14-fs probe pulse used for the pump-probe measurements (dashed and dotted curves, respectively).

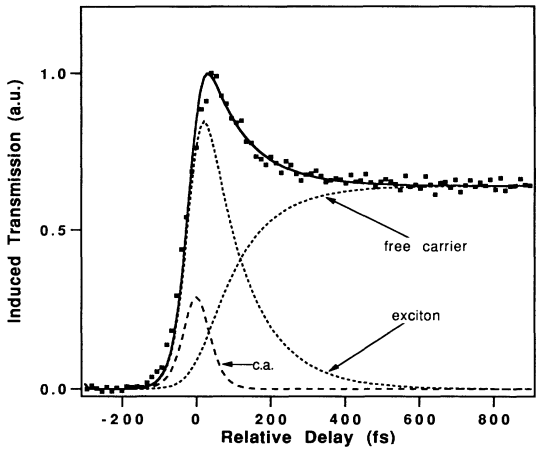

FIG. 2. Room-temperature pump-probe response measured at 620 nm using lock-in detection (see description in text). Experimental (points) and calculated (smooth solid curve) pump-probe response using the rate equations and parameters given in the text. The separate contributions of excitons and free carriers are shown as dashed lines. Each response is the sum of a pure decay term and a coherent artifact term. The total coherent artifact term is shown separately.

plified by a copper-vapor-laser-pumped amplifier operating at an 8.5-kHz repetition rate [9]. The amplified pulses, of duration 80 fs and center wavelength 624 nm, overlap spectrally with the low-energy side of the ground-state excitonic absorption peak. One portion of the amplified beam, after attenuation to energies of about 1 nJ per pulse, is used to excite the sample. Another portion is spectrally broadened and compressed in a fiber-grating-prism compressor to measured durations of about 14 fs [9] (measured using the background-free autocorrelation technique). This latter pulse serves as a broad band probe of the dynamics in the quantum well, following excitation, with excellent temporal resolution. The probe is attenuated to energies at least 10 times less than that of the pump. The pump beam is focused to a 70-μm spot on the sample and the probe beam overlaps, in a smaller diameter, with the pump beam. The pump-probe data are acquired by two different modes. In one set of experiments, the probe transmission spectra, as a function of relative delay between the pump and the probe, are spectrally resolved with an optical multichannel analyzer. In another set of experiments, the transmitted probe signal is detected by a silicon detector with a narrow band (10 nm) filter, followed by a lock-in amplifier.

Figure 2 shows the room-temperature differential transmission pump-probe data at the excitonic resonance. Initially, only excitons are resonantly created by the 80-fs pump beam. The density of carriers generated is estimated to be about 7×10^{11} cm^{-2}. The change of transmission induced by the created carriers is traced by the 14-fs broad band probe pulse as a function of delay. A 620-nm filter was employed, after the sample, to spectrally select the transmitted probe signal without sacrificing the temporal resolution. As the density of carriers (excitons or free e-h pairs) increases, the oscillator strength and thus the absorption strength decreases, due to screening and phase-space filling [5]. In the low excitation regime, we can express the differential transmission as [5] $\Delta T/T \propto (R_{eh/\mathrm{exc}}N_{\mathrm{exc}}+N_{eh})$, where N_{exc}, N_{eh}, and $R_{eh/\mathrm{exc}}$ are the exciton density, density of uncorrelated e-h pairs, and the ratio of bleaching strength of excitons to that of free e-h pairs, respectively. In the induced transmission spectrum shown in Fig. 2, the fast component, for delays less than 300 fs, corresponds to the dynamic bleaching of excitonic absorption due to the resonantly created excitons. The fast recovery of the absorption is mainly due to the exciton ionization through LO phonon scattering. The slow component, for delays longer than 300 fs, corresponds to the absorption bleaching by the ionized electron-hole pairs, with a relatively long recombination time. When the generated carrier density is increased from 7×10^{11} to 2×10^{11} cm^{-2}, the time-resolved differential transmission is essentially unchanged.

The exciton dynamics can be modeled using the following rate equations:

$$\frac{dN_{\mathrm{exc}}}{dt}=G_{\mathrm{exc}}(t)-\frac{N_{\mathrm{exc}}}{\tau}, \tag{1}$$

$$\frac{dN_{eh}}{dt}=\frac{N_{\mathrm{exc}}}{\tau}, \tag{2}$$

where $G_{\mathrm{exc}}(t)$ is the exciton creation rate by the pump beam, and τ is the exciton ionization time. Here, we assume that the pump beam generates only excitons and the free e-h pairs are created only through the ionization of the resonantly created excitons. This assumption is quite appropriate in the present case, since the excitonic peak is well separated from the continuum due to the large exciton binding energy, E_x^b (≈ 23 meV) [7], and the pump spectrum overlaps with the long-wavelength side of the

absorption peak (see Fig. 1). Equations (1) and (2) are integrated (using a finite-duration pump and probe pulse) to obtain the pump-probe response as a function of the relative delay between the pump and probe pulses. The "coherent artifact" term, which arises from terms in the third-order polarization that do not result from a pump-induced population, is usually present in the pump-probe measurement [8]. The coherent artifacts for both excitons and ionized *e-h* pairs were also calculated from Ref. [8], and added to the transmission change produced by the induced exciton and free carrier populations, to obtain the full pump-probe response. The points in Fig. 2 represent the experimentally observed response at 620 nm and the solid line is obtained from the calculations, using an 80-fs pump pulse, a 14-fs probe pulse, an exciton ionization time $\tau = 110 \pm 20$ fs, and the ratio $R_{eh/\mathrm{exc}} = 1.8 \pm 0.2$. The calculated curve is in excellent agreement with the observed data. The fitted exciton ionization time agrees very well with estimates from the homogeneous linewidth broadening [7]. The exciton ionization time of 110 fs is significantly faster than 300 fs of GaAs QWs [4], as expected from the stronger exciton-LO-phonon interactions in wide-gap II-VI QWs. The fitted absorption bleaching ratio $R_{eh/\mathrm{exc}}$ of 1.8 means that the bleaching due to resonantly created excitons is almost 2 times stronger than that due to the same number of uncorrelated *e-h* pairs at room temperature.

The pump-probe spectra were also spectrally resolved with an optical multichannel analyzer, by taking advantage of the broad bandwidth of the ultrashort probe pulse. Figure 3 shows the spectra, plotted as $\Delta T/T$, at various delays between the pump and the probe. The excited carrier density is estimated to be about 7×10^{11} cm^{-2}. The

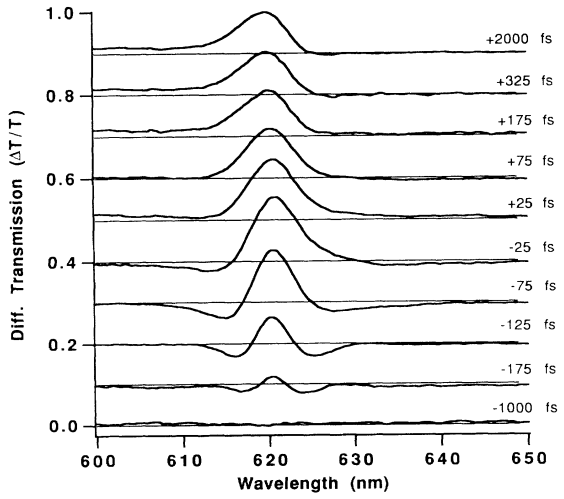

FIG. 3. Spectrally resolved pump-probe response of the CdZnTe/ZnTe quantum wells in the vicinity of the room-temperature excitonic resonance, at various relative delays between pump and probe, plotted as $\Delta T/T$. Each curve is displaced by 0.1 along the vertical axis.

biggest change of transmission is observed near zero delay at the excitonic absorption peak and its magnitude decreases rapidly until about 200 fs, with no further significant change after, consistent with the result in Fig. 2. At early times, we observe an oscillatory structure, which is consistent with previous calculations of nonlinear effects in pump-probe measurements [10]. Moreover, it is interesting to note that at negative times the observed spectral asymmetry in the oscillatory structure is in very good agreement with the simulation shown in Fig. 3 of Ref. [10], for the case of a detuned pump pulse. We also observe an increase of the transmission in the continuum around 610 nm, which should result from the increased population of the ionized carriers in that spectral range. This heating-up process is already near equilibrium at 175 fs. At substantially long delays (+2 ps), we consistently find an increased absorption around 625 nm, which indicates broadening of the excitonic peak, in addition to the bleaching.

In quasi-2D QWs, the exciton saturation due to long-range Coulomb screening is considered to be much weaker than that due to the effects of the Pauli exclusion principle (the phase-space filling and exchange interaction) [2,5,11]. This is supported by reasonable agreement between the experimental results of excitonic absorption bleaching in III-V MQWs and theories based only on the Pauli exclusion principle. For an accurate comparison of the bleaching effect due to excitons and free carriers, the room-temperature femtosecond exciton ionization measurement is very reliable, especially when the effects are comparable, since the effects of the same density of excitons and free carriers can be compared directly in one time-resolved experiment. For III-V MQWs, the ionized *e-h* pairs, with one LO phonon absorption, are initially hot ($kT/E_x^b \approx 3$–10), with excess energies larger than 25 meV and remain hot since $kT_L \approx 26$ meV. A stronger excitonic absorption bleaching by excitons than by the same number of free *e-h* pairs is observed in this situation. This observation was interpreted in terms of a strongly reduced band filling effect by hot free carriers due to the reduced occupation of the phase space sampled by the exciton, whereas the phase-space filling effect due to the cold excitons is large [5].

In marked contrast, the present CdZnTe/ZnTe QWs provide a unique situation, in which $E_x^b (\approx 23$ meV$) \approx kT_L \approx h\nu_{\mathrm{LO}} (\approx 25$ meV$)$. In this case, the ionized *e-h* pair from the resonantly created exciton is initially cold, with an excess energy of about 2 meV. Additionally, at room temperature ($kT_L \approx 26$ meV), the ionized carriers possess a relatively small kT/E_x^b (≈ 1) even at equilibrium, or, equivalently, the carriers are cool in units of kT/E_x^b at equilibrium. For $kT/E_x^b \approx 1$, a theoretical estimate [5] predicts that the bleaching of excitons by excitons is much less effective, by a factor of 0.5, than that by free *e-h* pairs. However, the measured bleaching strength of resonantly excited excitons in the present case is, surprisingly, 1.8 times stronger than that due to the same

number of cool free *e-h* pairs. The bleaching strength is in disagreement with that predicted in Ref. [5], which is calculated in the limit of $T=0$ and $T=\infty$ K and extrapolated between them to obtain a value for $kT/E_x^b \approx 1$. Our result, however, strongly supports the assumption that long-range Coulomb screening is negligible in quasi-2D MQWs, since otherwise the bleaching due to cool free carriers, which is supposed to screen most strongly in the bulk, would overwhelm that due to excitons.

The time resolution afforded by the 14-fs probe pulses allows us to rule out a significant contribution to the bleaching from "cold" free carriers. Attempts to fit the present data, in the framework of Ref. [5], can be done by two possible mechanisms, both of which can be invalidated experimentally. In the first mechanism, cold excitons are instantaneously ionized into cold free carriers by one LO phonon absorption. The free carriers become warm by absorbing another LO phonon. Following Ref. [5], the peak in the induced transmission (bleaching) is due to the initially cold ionized *e-h* pairs, which bleach most strongly, while the decay is due to the warming of these *e-h* pairs by LO phonon absorption, which bleach relatively weakly. Even though this mechanism can be fitted to the present data, the instantaneous exciton ionization is unreasonable when one considers the measured finite homogeneous absorption linewidth. In fact, the 110-fs decay of the induced transmission is in excellent agreement with the homogeneous exciton linewidth broadening, which assumes the ionization of excitons through LO phonon scattering. In the second mechanism, cold free carriers are assumed to decay into warm or cool carriers in a finite time (about 100 fs). This process involves three steps, first the generation of excitons via resonant excitation, second the creation of cold free *e-h* pairs through exciton ionization with an LO phonon, and finally warming of the resultant cold free carriers with another LO phonon absorption. The rise time of the induced transmission peak would then be significantly lengthened, assuming the prediction of Ref. [5] that cold free carriers bleach twice as strongly as excitons. With our time resolution, this lengthened rise time would be clearly observable. In fact, the observed rise time is about 90 fs, which corresponds well to the integration of an 80-fs pulse.

With all of these considerations, the measured $R_{eh/\mathrm{exc}}$ ($=1.8$) should reflect the fact that the absorption bleaching of the excitonic resonance due to cold excitons is stronger than that due to the same number of cool uncorrelated *e-h* pairs. A recent, more rigorous extension of Ref. [5] which has been performed by Zimmermann [11] has shown better agreement with the experimental results in III-V MQWs. This theory [11] also predicts the stronger exciton bleaching by resonantly excited excitons than that by the same density of cool free *e-h* pairs, by a factor of 1.2. This value is an improvement over the value of 0.5 predicted using Ref. [5]. However, the present discrepancy ($R_{eh/\mathrm{exc}}=1.2$ vs 1.8 ± 0.2) still requires further investigation.

In summary, we have found the initially unexpected result that the bleaching effect of cold excitons on excitons is stronger than that of the same density of cool uncorrelated *e-h* pairs in quasi-2D MQWs. While this finding strongly confirms the argument of negligible long-range Coulomb screening in quasi-2D MQWs, it also points out the gap in the theory. The wide-gap II-VI CdZnTe/ZnTe MQWs, which show well-defined room-temperature excitonic absorption peaks, are uniquely qualified for this study, since E_x^b, $h\nu_{\mathrm{LO}}$, and kT_L are all comparable in this system and as a result, the ionized *e-h* pairs have very small excess energies. The employed broad band 14-fs probe pulses are critical to unambiguously elucidate the ultrafast dynamical events induced by 80-fs pump pulses. We have measured a very fast exciton ionization time, 110-fs, which agrees well with estimates from the homogeneous linewidth broadening, supporting a model of thermal broadening due to the ionization of excitons through LO phonon scattering. This exciton ionization time is significantly faster than that reported in III-V quantum wells, reflecting the stronger exciton–LO-phonon interaction in this wide-gap II-VI MQW system.

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