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Hot-exciton luminescence in ZnTe/MnTe quantum wells

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Hot-exciton luminescence phenomena are investigated in a ZnTe/MnTe single-quantum-well structure where tunneling through thin MnTe barriers suppresses the formation of thermalized luminescence. The longitudinal-optical-phonon-modulated recombination spectra are excitonic in nature and show strong resonance enhancement at energies that lie within localized states below the $n=1$ exciton.

Hot luminescence (HL) and resonant Raman scattering (RRS) are two processes where, following initial photoexcitation above the band gap of a semiconductor, the reemitted photons show spectral features that are (i) modulated by the energy of an elementary excitation (most commonly optical phonons) and (ii) are strongly enhanced at the band gap E_g in a direct-gap material. Some time ago, the question of separating these two processes was subject to considerable debate and study (e.g., Refs. 1–3). Following the definition, e.g., by Takagahara,[4] RRS can be viewed as a one-step coherent process where the observed emission spectrum is precisely correlated with incident light in terms of the energy of excitation and polarization (in steps of the phonon energy), whereas HL is a multistep sequential process where additional scattering is present in such a way that the spectrum is still energetically correlated with respect to the photon energy of excitation, but carries very little or no polarization (i.e., phase) memory. In a polar crystal the RRS and HL processes are both dominated by the Fröhlich interaction, i.e., the coupling of the photoexcited electron-hole pairs to the longitudinal-optical (LO) phonon.

In this paper we study the details of the HL process in a contemporary context, namely that of a II-VI compound semiconductor quantum well (QW) where (a) the fundamental absorption edge is strongly excitonic by confinement enhancement, and (b) the structures can be designed to enhance the observation of HL and RRS phenomena. By following the details of the emission spectra with increasing number of optical phonons participating, we see the clear delineation of the HL process from RRS. We show experimental results in high magnetic fields which emphasize the role of "hot" excitons over free-electron–hole pairs throughout the LO-phonon-intermediated energy-relaxation process. Among earlier experimental and theoretical efforts in the 1970s, whose aim was to study the details of such strongly coupled electronic and lattice excitations in bulk materials, we note here the work by Klochikhin, Morozenko, and Permogorov[5] in ZnTe, the semiconductor used here as well. In QWs which mimic a quasi-two-dimensional (2D) system, there is the issue of additional weak disorder which originates from QW-thickness fluctuations (on monolayer scale) as well as compositional disorder at interfaces (finite chemical intermixing). Such disorder has been found in many different QW systems to induce to exciton-localization effects below some form of mobility edge in the joint conduction-valence band density of states. Below, we demonstrate the influence of finite disorder on the details of the HL resonance enhancement and find that localized states play an important role.

Our focus here are on experimental results obtained on a single-QW (SQW) structure of MnTe/ZnTe, consisting of 22-Å-wide MnTe barrier layers [$E_g \sim 3.20$ eV (Ref. 6)] and a 47-Å-thick ZnTe QW, the dimensions measured by transmission electron microscopy (TEM). The SQW is grown by molecular-beam epitaxy[7] on a buffer layer of ZnTe and a GaSb substrate; the latter two are nearly lattice matched ($\delta a/a \sim 0.1\%$). While MnTe crystallizes as a hexagonal layered crystal in bulk form, it has been recently shown that good quality epitaxial layers in cubic zinc-blende structures can be realized.[7] Apart from other considerations, the choice of a SQW structure with relatively thin constituent layers was necessary to ensure a pseudomorphic structure in light of the large lattice mismatch between ZnTe and zinc-blende MnTe of approximately 4%. Raman-scattering measurements,[5] confirmed by the absence of misfit-induced dislocations in TEM images, indicated that the strain is then accommodated pseudomorphically in the MnTe layers and that the degree of chemical intermixing at the ZnTe/MnTe interfaces is approximately one monolayer. Reflectance and first-order RRS spectroscopy showed a well-defined $n=1$ exciton QW resonance (heavy hole, hh) at $E_{gx} \sim 2.49$ eV, with an approximate linewidth of 10 meV (see portion of the reflectance spectrum in the inset of Fig. 1). We have used the measured heavy-hole–light-hole splitting in variational calculations[8] to estimate the valence-band offset $\Delta E_v \sim 100$ meV and the heavy-hole-exciton binding energy of $E_g \sim 25$ meV. (For reference, the bulk-exciton band gap in ZnTe is 2.39 eV with a binding energy of approximately 11 meV.) A key experimental point is that because of the thin MnTe barrier layers, significant tunneling of electron-hole pairs from the QW was expected to occur on the picosecond time scale. In the event, slower energy-relaxation processes which lead to the build up of thermalized luminescence in the QW were substantially

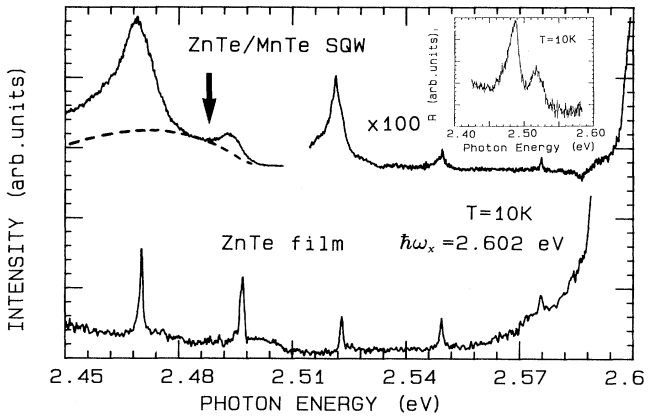

FIG. 1. Comparison of secondary emission spectra from the ZnTe/MnTe SQW and an epitaxial ZnTe thin film at $T=10$ K, photoexcited at $\hbar\omega_{ex}=2.602$ eV (residual laser scatter in the figure). Note the amplitude scale-factor change in the upper trace. The $n=1$ hh exciton resonance is marked with an arrow and the background thermalized luminescence is indicated by the dashed line in the upper trace to guide the eye. The vertical lines are separated by the bulk ZnTe LO-phonon energy. The inset shows portion of the reflectance spectrum.

short circuited. As a consequence, our emission spectra in the band-edge region were dominated by the HL *or* RRS processes at all measurement temperatures reported here. Also recall that ZnTe is a rather polar semiconductor with strong Fröhlich interaction; e.g., the electron-LO-phonon (polaron) coupling constant is $\alpha\sim0.30$ in bulk ZnTe, compared with that of GaAs $\alpha\sim0.07$. This leads to ready experimental observation of high-order HL processes. In our QW samples, more than 14 orders of LO scattering could be observed! We note here that hot-exciton effects in coupled GaAs/(GaAl)As QWs have been recently seen, also as a result of rapid tunneling processes.[9] Studies of exciton relaxation and HL in conventional (Cd,Zn)Te QWs are also being pursued.[10]

In Fig. 1 the emission spectrum of the ZnTe/MnTe SQW at $T=10$ K is compared with a thin film of ZnTe under the same conditions of photoexcitation (at $\hbar\omega_{ex}=2.602$ eV) in a backscattering configuration ($zxx\bar{z}$, where z is the [001] crystalline direction and $x=[110]$). The arrow identifies the absorptive $n=1$ hh-excitonic resonance as obtained from reflectance (inset) and 1st-order RRS spectra (see below). The dominant features in the band-edge emission of the SQW for this $\hbar\omega_{ex}$ are the 4th- and 5th-order phonon sidebands (henceforth denoted by 4LO and 5LO, respectively), superimposed on a relatively weak and broad residue of the thermalized luminescence background (dashed line in Fig. 1). A substantial Stokes shift (~15 meV) between the resonantly enhanced emission maximum and the absorptive $n=1$ exciton edge is evident. Apart from the strong resonance enhancement by about *three* orders of magnitude, note also the linewidth increase with increasing order of scattering (see also Fig. 4 below). At the same time, we measured a gradual loss of polarization memory starting from a polarized 1LO to an unpolarized 5LO line. This is in contrast to the epitaxial film of ZnTe where all orders shown in Fig. 1 have almost the same narrow linewidth (≈1 meV) and remain polarized. (Note however that for the film we are still well above the excitonic band-gap resonance; intense thermalized luminescence prevented us from observing the phonon features at lower photon energies.) We interpret this to indicate that the coherence of a RRS process is weakened in the SQW with additional scattering so that the higher-order phonon lines are indeed more appropriately termed as being due to HL.

One key argument from theoretical grounds separating the HL and RRS processes is that they should exhibit distinctly different time-dependent behavior,[1] a point of particular interest here for the 2D exciton systems in a QW structure. We have performed time-resolved experiments by using mode locked dye-laser pulses of approximately 2 psec in duration as a source of excitation and a monochromator-streak camera system for time-resolved spectroscopy. In the upper trace of Fig. 2 the transient intensity of the 5LO peak of Fig. 1 at $T=10$ K is shown for excitation at photon energy $\hbar\omega=2.602$ eV. The lower trace shows the system time resolution to the incident laser pulse. The exposure time for both spectra was adjusted to be identical so that any possible effects from intensity-dependent timing jitter and dark counts could be eliminated. The transient emission of the 5LO peak can clearly be resolved with a decay time of approximately 10 psec, distinctly longer than, e.g., a 1LO phonon line. Hence, we have also time-resolved evidence for the assumption that a HL—not a Raman process—is the mechanism for the secondary emission here.

One controversial issue in the interpretation of HL phenomena in the bulk concerned the role of the electron-hole Coulomb interaction in the process, namely whether the LO-phonon-intermediated energy relaxation involves a Coulomb-correlated pair, i.e., a hot exciton, or independently relaxing electrons and holes (e.g., Ref. 5). To investigate this question in a ZnTe QW (with an estimated enhancement to the exciton binding energy by more than a factor of 2), we studied our HL spectra in perpendicular magnetic fields up to 23 T. Figure 3 shows the recombination spectra near the $n=1$ resonance in fields of $B_z=0$, 10, and 23 T. Due to the small but finite chemical intermixing in the SQW structure, a region of diluted

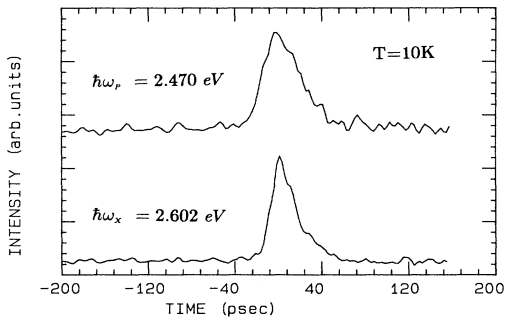

FIG. 2. Time-resolved emission of the 5LO peak of Fig. 1 at $\hbar\omega=2.470$ eV (upper trace), following excitation by a picosecond laser pulse at $\hbar\omega=2.602$ eV. The lower trace shows the system time resolution as a response to the exciting pulse. The time origin is chosen at the peak of the excitation pulse.

magnetic semiconductor (DMS) $Zn_{1-x}Mn_xTe$ exists at the heterointerfaces with a steep (monolayer) concentration gradient. While MnTe is an antiferromagnetic semiconductor at low temperatures, the DMS portion, into which wave functions of electron-hole pairs readily reach, produces a Zeeman redshift of the excitonic gap (by analogy to well-established behavior in bulk DMS crystals). At a field of $B=10$ T this exchange effect with the Mn-ion d-electrons has caused the reduction in the 4LO amplitude ($m=4$) by the reduction in the resonance energy, and a corresponding increase of the 6LO line ($m=6$). Beyond ~ 10 T the DMS effect saturates (from nearly paramagnetic behavior), at least to the point of canceling diamagnetic shifts, and the entire emission spectrum remains unaltered up to the highest fields available to us, as shown in the resonance region in Fig. 3. This key observation is taken by us to be a direct indication of the excitonic nature of the HL emission. At $B=23$ T the free-electron cyclotron energy in ZnTe is approximately 25 meV, i.e., comparable to the LO-phonon energy and the exciton binding energy. If independent free-electron and hole "energy relaxation" with LO phonon steps were the dominant process, strong effects due to orbital quantization would have been expected to modify the spectra. In analogy to magnetic-field effects in thermalized recombination of quasi-2D excitons in QW,[11] we postulate that the Coulomb correlation dominates in our case throughout the hot-exciton energy range (~ 100 meV or more).

We now turn our attention to some of the details in the resonance-enhancement process. The close relationship between scattering and finite disorder near the $n=1$ exciton resonance in our quasi-2D system is based on two key empirical observations. First, the strong resonance enhancement is maximized below the absorptive $n=1$ exciton resonance in the energy range where the density of states is of localized character. Second, whereas in the bulk epitaxial film all orders m in the phonon sidebands occur according to the precisely fixed energetic step of one LO-phonon energy at $\mathbf{q}\approx 0$ of ZnTe [$\Delta E(m,m-1)=\hbar\omega_{LO}=26.4$ meV] in the range of photon energies studied, pronounced deviations from such a precisely defined energy ladder up to ~ 2 meV are seen in the SQW case as we approach the $n=1$ excitonic resonance. Some of this deviation is very likely due to additional scattering and localization processes which break the **k**-conservation rule and allow for the participation of optical phonons over much of the bulk LO-phonon dispersion curve.

Our studies strongly suggest that the energy range in the middle of the background thermalized luminescence, i.e., localized states in the disorder-induced density-of-states tail, also acts as a center of "gravity" for the HL enhancement process once a transition from the RRS regime is substantially completed (i.e., the process is of sufficiently high order). We confirmed this by "excitation spectroscopy" where the intensity of the mth-order LO-phonon emission peak was monitored with tuning of the photon energy of excitation. The energy position of the mth-order LO line at its maximum intensity is shown as a function of order in Fig. 4, measured with respect to the resonance of the first-order RRS spectrum (at 2.493 ± 0.003 eV). The figure also shows the increase in the linewidth of the resonantly enhanced emission peak with increasing order, from $\Delta E\approx 1.6$ meV for the 1LO line to $\Delta E\approx 10.6$ meV for the 5LO line at resonance. The first-order line (1LO) was clearly Raman-like with well-defined polarization-selection rules and the excitation maximum is very near the reflectance maximum of the $n=1$ resonance. From Fig. 4 it is clear that as the order m increases, the maximum in the resonance enhancement redshifts monotonically.

Further supporting these ideas, we have found that the details of the $\Delta E(m,m-1)=\hbar\omega_{LO}$ deviation are very complex near the resonance, with sensitive dependence on both the photon energy of excitation and temperature in the resonance region. We show one example in Fig. 5, where the 5LO and 6LO spectra are displayed for two different excitation energies, $\hbar\omega_{ex}=2.632$ eV and $\hbar\omega_{ex}=2.619$ eV. The corresponding $\Delta E(m=6,5)$ are 22.2 and 25.4 meV, respectively. For example, $\Delta E(m=6,5)$ is minimum when the 6th-order sideband is at the center of thermalized luminescence, that is, in the energy range where the maximum hot-exciton population is realized in

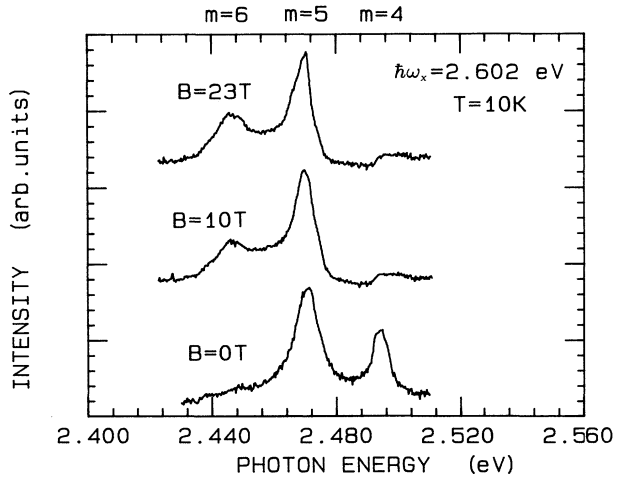

FIG. 3. Magnetic-field dependence of the HL emission up to 23 T in the region near the $n=1$ exciton resonance at $T=10$ K.

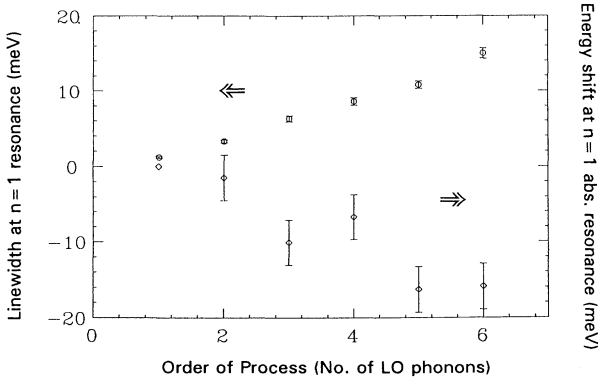

FIG. 4. Shift of the resonance enhancement with increasing order in the LO-phonon-intermediated secondary-emission process (right-hand side). Also shown is the increase in the linewidth at the corresponding emission maximum (left-hand side). The energy scale applies for both axes.

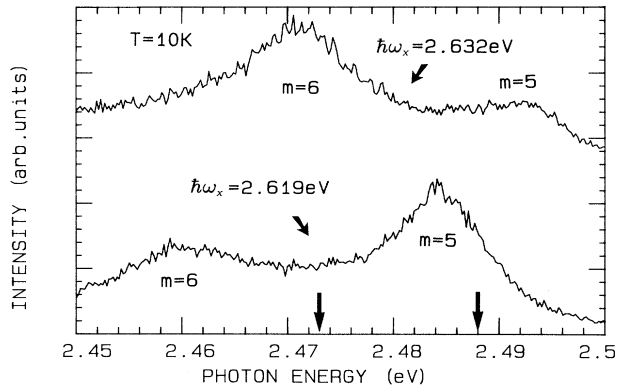

FIG. 5. Dependence on $\hbar\omega_{ex}$ of the HL spectrum for the 5LO and 6LO lines near the resonance regime (arrows show the absorptive $n=1$ excitonic gap and the center of gravity for the background thermalized luminescence, respectively).

the localized density-of-states tail in the QW. Similar effects were found for other higher orders in the resonance region (typically for $m \geq 4$).

Temperature dependence of the HL adds insight into the details of the resonance enhancement and the role of the localized states while further emphasizing the contrast with the RRS process. In the upper portion of Fig. 6, we show the spectra of Fig. 1 at several different temperatures. In the range from 10 to 70 K we observe a near collapse of the 4LO line while the 6LO peak actually grows. This is as expected from the thermally induced shrinkage of the bandgap (≈ 12 meV for this range) and the corresponding shift in resonance enhancement. Notice, however, that the amplitude of the 5LO line remains nearly unchanged and that there is also a *blueshift* of ≈ 3 meV. The behavior in the higher-temperature interval $T=70$–110 K is more striking. The 5LO line now quenches rapidly but also redshifts at a rate very nearly equal to $\Delta E_g/\Delta T \sim -0.4$ meV/K. Meanwhile, the energy difference between 6LO and 5LO becomes as small as 12 meV whereas the energy difference between 5LO and 4LO peaks increases up to 40 meV (recall that $\hbar\omega_{LO}=26.4$ meV). Hence the HL spectra still do show an adherence to the photon energy of excitation but clearly the tracking by the mth-order phonon lines of $\hbar\omega_{ex}$ softens with increasing temperature in the resonance region. We interpret this behavior qualitatively as a gradual transition from purely HL regime to a quasithermal regime where additional scattering brings about a complicated hot-exciton energy-relaxation sequence near the vicinity of the mobility edge where localized states are important participants in the overall relaxation process. As a comparison,

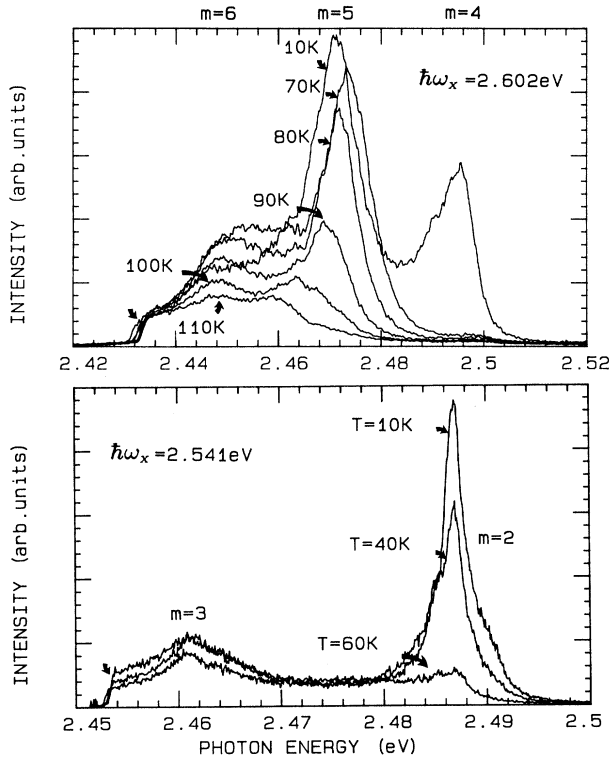

FIG. 6. Temperature dependence of different LO-phonon lines in the resonance enhancement regime. Upper trace: 4LO, 5LO, and 6LO lines. Lower trace: 2LO and 3LO lines.

the lower portion of Fig. 6 shows the temperature dependence of the lower-order phonon-emission peaks near the bandgap resonance for the 2LO and 3LO lines. Apart from amplitude variations associated with the band-edge redshift (and hence in resonance-enhancement energies), no anomalies in the departures from strict LO-phonon energy demarkation were observed. (Same behavior was also verified for the 1LO and 2LO lines.) This shows that the lower orders ($m<4$) are near or at the RRS limit and are largely unaffected by the details of complex scattering near the delocalized-localized states boundary.

In summary, studies of HL in a ZnTe/MnTe QW have yielded insight into the role of disorder and excitons in a process whose details are sensitive to the number of LO-phonon modes involved, temperature, and the relaxation kinetics within localized exciton states.

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