PHYSICAL REVIEW B **79**, 241310(R) (2009)

Giant modulation of resonance Raman scattering from (Cd,Mn)Te quantum wells by secondary illumination

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(Received 21 May 2009; published 12 June 2009)

Large changes in the intensity of spin-flip Raman signals from (Cd,Mn)Te quantum wells arise under weak additional illumination above the barrier band-gap energy even when the secondary beam is 2 orders of magnitude weaker than the beam used to excite resonant Raman scattering. The behavior is ascribed to changes in the lifetime of the intermediate state in the Raman-scattering process caused by the light-induced alterations in the quantum well carrier density; spin-flip Raman scattering is highly sensitive to this since it is a doubly resonant process.

DOI: 10.1103/PhysRevB.79.241310 PACS number(s): 78.30.−j, 73.63.Hs, 75.50.Pp, 78.67.De

Spectroscopy of the near-band-edge optical features in semiconductor nanostructures can provide vital information about symmetry, band structure, and electronic properties. In such studies, one often modifies the behavior of the sample by applying magnetic or electric fields or by changing the temperature. A further possibility is to illuminate the specimen with a secondary light beam with a photon energy above the band gap of the barrier material so as to alter the concentrations of free charge carriers.[1–3] This provides an elegant means to modify the excitations of a two-dimensional electron gas within a quantum well.[4,5] Also, mobile photogenerated carriers will partially screen the built-in electric fields in a heterostructure, thus, affecting its optical reflectivity; photomodulation is a powerful tool since background features are eliminated[6–9] though the changes ΔR in the reflectivity R induced by the secondary illumination are usually small ($\Delta R/R \sim 10^{-4}$).

Here, in contrast, we describe the unexpected effects that such illumination can have on the resonant spin-flip Raman scattering (SFRS) from a quantum well (QW). We have observed order-of-magnitude changes in the intensity of the SFRS signals even when the secondary beam was as much as 2 orders of magnitude weaker than the primary beam. The changes in the SFRS are accompanied by much smaller fractional changes in the photoluminescence (PL) and reflectivity. We show that the behavior is caused by alterations in the nature of the intermediate state of the scattering process. Our results provide insight into the way in which secondary illumination affects Raman-scattering processes in particular and optical spectroscopy in general; it appears that this effect provides a valuable spectroscopic and diagnostic tool. Although we report here on CdTe-based heterostructures, the photomodulation effects described above are common to many materials [e.g, GaAs, ZnSe, and CdTe (Refs. 1–9)] and we expect this to be true also of the effects we describe.

The (Cd,Mn,Mg)Te heterostructures were grown by molecular-beam epitaxy on (001) GaAs substrates. We discuss two samples (representative of several studied). Sample 1 contained four CdTe quantum wells (widths from 20 to 80 Å), with $Cd_{0.5}Mn_{0.5}Te$ barriers (widths 500 Å, band gap 2.39 eV). Sample 2 had one CdTe QW (width 71 Å) and [(Cd,Mn,Mg)Te barriers, band gap 2.05 eV]. For SFRS, the magnetic field (up to 6 T) was in the QW plane; the samples were held at 1.6 K and a Ti;sapphire laser provided the primary tunable excitation. For the secondary beam, we used, variously, a He-Cd laser (442 nm), the blue/green lines of an Ar^+-ion laser, or a He-Ne laser (633 nm). Raman and PL spectra were recorded by a triple spectrometer with the charge-coupled device detection. For PL excitation (PLE) spectroscopy, the low-energy tail of the PL was monitored with an avalanche photodiode.

In the PL and Raman experiments, the intensity of the focused primary beam was typically ~ 10 W cm^{-2}. The secondary (blue) beam exceeded the primary spot in size and its intensity was 1–4 orders of magnitude smaller than that of the primary beam. In all the present experiments, the blue beam, when applied *alone*, produced a QW PL intensity whose magnitude was vanishingly small compared to that produced by the red beam. The changes in the reflectivity that were induced by unfocused blue illumination were recorded using an incandescent lamp as the light source filtered to remove the high-energy part of the spectrum.

The main SFRS signals in Fig. 1 with crossed linear excitation and detection polarizations correspond (i) to the spin flip of a conduction-band (CB) electron in the QW, (ii) to a spin flip of a 3*d* electron located on the Mn^{2+} ion [paramagnetic resonance (PR)],[10,11] and (iii) to overtones of the PR signal (2PR). The Mn^{2+} 3*d* electron has a *g* factor of 2.0, while the CB electron has a *g* factor which is enhanced by the *s-d* exchange and which therefore depends on the QW width and on the Mn concentration in the barriers.[12] Both signals (i) and (ii) demonstrate resonant behavior when the excitation is tuned either to the neutral QW exciton state (X) or to the negatively charged trion (T).[10]

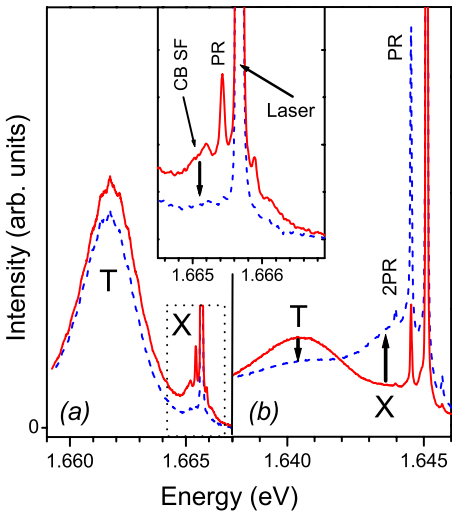

FIG. 1. (Color online) Effects of the secondary (blue) illumination on the PL and SFRS spectra from two CdTe/(Cd,Mn,Mg)Te QWs (a) sample 1 and (b) sample 2. Solid lines: primary (red) illumination only; dashed lines: blue light also present. The inset shows an expanded view of the region within the dotted box. The vertical arrows show the effects of the blue illumination.

Our central observations are illustrated by Fig. 1, which shows the PL and Raman signals when the primary beam is tuned to the neutral exciton (X) state. In Figs. 1(a) and 1(b), SFRS signals appear on either side of the laser line; in addition, the trion-related PL bands appear at 1.662 and 1.6405 eV, respectively. The effects of the blue beam are shown by the broken curves. The SFRS intensity undergoes dramatic and sample-dependent changes. It almost disappears in the case of sample 1 [Fig. 1(a)] but increases by five times in the case of sample 2 [Fig. 1(b)]. Blue illumination also modifies the PL intensity though less strongly than it does the SFRS spectra; in Fig. 1(b), for example, it is clear that the trion PL is halved while the exciton PL becomes much stronger.

Though additional illumination could lead to heating,[13] we rule this out here because (i) it is unlikely that heating could cause large changes in the opposite sign for two similar QWs and (ii) no changes in the Raman shift of the electron SFRS line were observed despite the fact that the g factor of the CB electrons in dilute magnetic semiconductor heterostructures [in our case, (Cd,Mn)Te] is strongly temperature dependent.[12]

For all samples, the changes in the SFRS are similar in both (π,σ) and (σ,π) polarization configurations and for all magnetic fields up to 6 T. Strong responses occur only for secondary illumination with photon energies above the barrier band gap.

Figure 2 shows the resonance profiles of the SFRS lines for sample 1 with and without a blue beam (80 mW cm^{-2}). Both the CB electron and the PR signals decrease markedly upon blue illumination when the primary laser is in resonance with the X state. In contrast, when the primary laser is in resonance with the T state, the quenching is much weaker. Figure 2(a) (inset) shows how the quenching depends on the blue beam intensity.

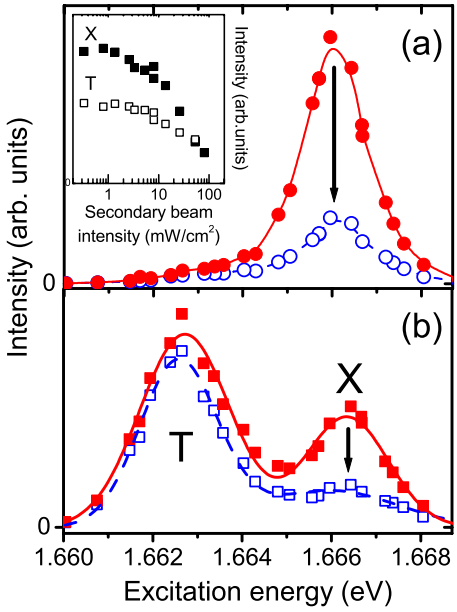

FIG. 2. (Color online) Intensities of the SFRS signals from one quantum well of sample 1 as a function of primary laser energy, with (hollow symbols) and without (solid symbols) secondary blue illumination for (a) the Mn^{2+} and (b) the electron SFRS signals. Lines are guides for the eyes. Peaks X and T correspond to the primary laser being tuned to the exciton and trion transitions, respectively. Inset: the Mn^{2+} SFRS signal intensity as a function of blue intensity, for the cases where the primary laser is in resonance with X and T.

A further feature is the effect that the secondary blue illumination has on the PLE spectrum. Figure 3(a) shows for sample 1 the excitation spectrum for PL detected at 1.660 eV (in the low-energy wing of the trion PL emission band). Open (closed) circles show the PLE spectrum with (without) the presence of a blue beam (40 mW cm^{-2}). Remarkably, the blue illumination causes a few percent decrease in the PL signal around the maximum accompanied by the slight increase in the wings [Fig. 3(a)]. This behavior is observed equally clearly with or without an applied magnetic field and is like that observed for CdTe/CdZnTe QWs.[14] By contrast, the blue beam quenches the reflectivity spectrum uniformly by a factor of ~1.5 [Fig. 3(b)] over the whole signal.

The main observations thus follow a hierarchy in which the blue secondary illumination affects the PLE spectrum weakly, the reflectivity moderately, and the SFRS very strongly. Perhaps the most remarkable result is that SFRS responses of the conduction-band electrons and of the Mn^{2+} paramagnetic resonance are both affected strongly by blue illumination when the primary laser is tuned to the energy of the exciton transition (X) but *not* when it is tuned to the trion energy. These observations lead immediately to the conclusion that the blue illumination affects specifically the X state.

The changes shown in Fig. 3(a) suggest a mechanism based on illumination-induced changes in the nonradiative contribution to the homogeneous linewidth of the X state. If the exciton state (at energy E_0) is inhomogeneously broadened (as is expected for a QW exciton), its net optical response $I(E)$ will be a convolution of the optical response of

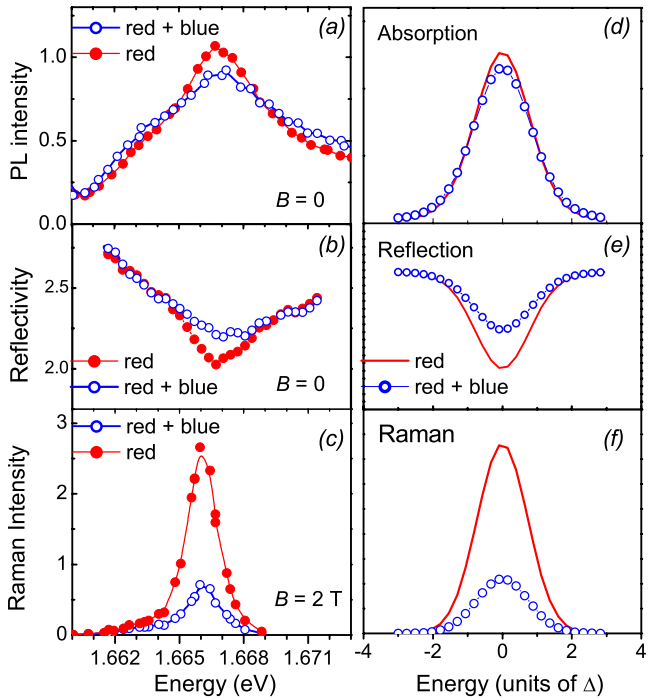

FIG. 3. (Color online) Parts (a)–(c) show, respectively, PLE, reflectivity, and SFRS signals for sample 1 without (solid symbols) and with (hollow symbols) secondary blue illumination. Vertical scales are in arbitrary units but with the same origins and scales. Parts (d)–(f) show the corresponding simulated responses (see text) without ($\Gamma/\Delta=0.2$, lines) and with ($\Gamma/\Delta=0.3$, lines plus points) a secondary beam.

the homogeneously broadened state $|M(E,E_{\rm res})|^2$ with the distribution of resonant energies $E_{\rm res}$ (Ref. 15); assuming a Gaussian distribution with an inhomogeneous linewidth Δ then

$$I(E) \propto \int_{-\infty}^{\infty} |M(E,E_{\rm res})|^2 \exp\left(-\frac{[E_{\rm res}-E_0]^2}{\Delta^2}\right) dE_{\rm res}. \quad (1)$$

For different optical processes, the elementary response shows different dependences on the full homogeneous linewidth Γ. For example, in absorption,[16–19]

$$|M(E,E_{\rm res})|^2 \propto \frac{\Gamma}{(E_{\rm res}-E)^2+\Gamma^2}, \quad (2)$$

where Γ accounts for both radiative and nonradiative processes. In reflectivity,[18–21]

$$|M(E,E_{\rm res})|^2 \propto \frac{1}{(E_{\rm res}-E)^2+\Gamma^2}. \quad (3)$$

Equation (3) holds also for the resonance Raman scattering mediated by optical phonons in which either the incoming or outgoing photon are in the electronic resonance.[15,22–24] However, in a SFRS process, *both* photons are in resonance; the doubly resonant scattering leads to

$$|M(E,E_{\rm res})|^2 \propto \left(\frac{1}{(E_{\rm res}-E)^2+\Gamma^2}\right)^2, \quad (4)$$

where for simplicity we assume Γ to be the same for both intermediate states. If the broadening of the X states is dominated by nonradiative processes, and if this broadening can be varied in some way by the blue beam, one obtains a simple result if $\Gamma \ll \Delta$. By substituting into Eq. (1), the values of $|M(E,E_{\rm res})|^2$ from Eq. (2), Eq. (3), or Eq. (4), one finds, respectively, that the absorption (and the PLE) should be independent of Γ, the reflectivity should depend on Γ^{-1}, and the SFRS on Γ^{-3}. This leads to the observed hierarchy of the blue beam effects and, in particular, to the giant sensitivity of the SFRS intensity to the blue beam. Further, if the magnitude of Γ is significant compared to that of Δ, a broadening of the PLE response would result, as is observed. Figure 3 exemplifies the results of a calculation with Eqs. (1)–(4) where we take the same values of Γ for reflection, PLE, and SFRS.

The main purpose of this work is to report the striking changes in SFRS on blue illumination and, by consideration also of the other optical spectra, to reveal the influence of the blue beam on Γ. However, it is interesting to discuss the underlying mechanisms for this influence. Illumination above the barrier band gap is known to modify the concentrations of the resident carriers in a QW.[14,16,25] Nominally undoped samples of the type studied here normally exhibit n-type background doping but changes in the substrate or surface conditions can reverse the intrinsic carrier type.[26] Trions of either sign can thus be observed, it being difficult to distinguish between them since they have similar binding energies.[2]

We thus infer that, in the dark, samples 1 and 2 have different types of carriers resident in the well. Illumination above the barrier band gap then adds carriers of one type into the QW, resulting in either an increase (sample 1) or a decrease (sample 2) in the resident carrier concentration. This in turn leads, respectively, to an increase (decrease) in the nonradiative contribution to the homogeneous linewidth of the X state.[27] The observed changes in the PLE line shape (Fig. 3) show that the homogeneous linewidth changes by about 0.4 meV, requiring the modulation of an exciton decay process with a lifetime τ on the order of picoseconds. It is well established that trapping of neutral excitons into trion states in such samples can be a suitably fast process [$\tau \sim 1-100$ ps (Refs. 28 and 29)] and is, of course, strongly dependent on the free-carrier concentration. The PL spectra themselves support the idea that trion formation is the dominant nonradiative decay mechanism for excitons since the ratio of exciton to total PL intensity (exciton plus trion) is given approximately by the ratio of the trion formation time to the exciton radiative lifetime τ_R. Since $\tau_R \sim 100$ ps,[30] the PL spectra of Fig. 1 are consistent with trion formation times of a few ps. This mechanism does not broaden the T states, which explains their much less-pronounced response to the blue illumination. The role of carrier injection is also supported by the fact that while in sample 1, on blue illumination, PL is still produced by the T state (carriers are available

to form trions); in sample 2 blue illumination enhances PL from the *X* state (due to a lack of carriers to form trions).

The large changes in the SFRS signals caused by the secondary illumination are due to their being doubly resonant and thus very dependent on the exciton linewidth. Such a sensitivity offers a means to monitor the fine control of the carrier concentration in a quantum well via secondary illumination and could provide a useful diagnostic technique for the determination of the carrier type of the dilute gas present in the dark.

A further important conclusion concerns the two-beam spectroscopy in general. When one beam is near resonance with an excitonic transition, the secondary beam can have a threefold influence on the QW luminescence. It can (i) supply electron-hole pairs to form neutral or charged excitons in the QW, adding to the overall PL signals, (ii) supply surplus electrons or holes, causing redistribution of intensity between the *X* and *T* lines, or (iii) change the absorption coefficient for the primary beam, causing a change in the overall QW PL signal. The possibility that each of these mechanisms is occurring must therefore be taken into account when interpreting such experiments.

This work was supported by the EPSRC (U.K.), INTAS under Grant No. 03-51-5266, the Foundation for Polish Science (subsidy 12/2007), and the Russian Foundation for Basic Research. We thank A. A. Klochikhin for useful discussions.

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