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Low-temperature anti-Stokes luminescence mediated by disorder in semiconductor quantum-well structures

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In low-temperature photoluminescence experiments on II-VI semiconductor quantum wells we find an energy transfer from confined quantum-well states to above-barrier states. The observed anti-Stokes barrier luminescence exhibits a characteristic intensity dependence showing that this transfer is caused by a two-step absorption process involving localized or impurity bound-exciton states in the quantum well. Time-resolved photoluminescence experiments show that the photon for the second intraband absorption step can be provided by the quantum-well luminescence, i.e., the anti-Stokes barrier luminescence is a direct consequence of photon recycling.

Anti-Stokes photoluminescence, i.e., emission that occurs at a wavelength shorter than the wavelength of the excitation source, has been observed in a variety of systems, such as atoms and molecules,[1–3] polymers,[4,5] fullerenes,[6–8] amorphous semiconductors,[9] and also in crystalline semiconductor heterostructures.[10] Even lasing on an anti-Stokes fluorescence line in rare-earth doped insulators is possible.[11] The commonly discussed microscopic mechanisms leading to anti-Stokes photoluminescence are Auger recombination,[12,13] thermal activation by the absorption of phonons, and participation of two (or more) photons in the optical excitation process.[1,10] There are two distinct mechanisms for the latter two-photon excitation process. First, the intermediate state is not real, i.e., the lifetime of an excitation in this virtual state is limited by the inverse energetic distance to the next real state. This purely coherent two-photon absorption (TPA) process must be distinguished from the second mechanism, a two-step absorption (TSA) process, where (i) the intermediate state is real and (ii) a relaxation of the excitation to lower-lying real states may occur before the second photon is absorbed.

In the case of crystalline bulk semiconductors and semiconductor heterostuctures, interband photoluminescence (PL) excited by TPA using photon energies well below the optical band gap is a well-known phenomenon,[10] the radiation of which exhibits a superlinear dependence on excitation intensity. Recently Tomita *et al.*[14] observed low-temperature anti-Stokes PL in asymmetric $GaAs/Al_xGa_{1-x}As$ double quantum-well (QW) structures. Optical excitation of the energetically lower-lying wide well exciton led to higher-energetic exciton luminescence from the adjacent narrow well, separated from the wide well by a thick barrier of $\geqslant 10$ nm. Most surprisingly, the authors found a linear intensity dependence of this anti-Stokes PL and excluded an indirect phonon-mediated or a direct TPA process as the responsible excitation mechanism. Dipole-dipole interaction between excitons of adjacent quantum wells[15] has been proposed to account for the excitation transfer between wells separated by thick barriers.[14] Since low-temperature anti-Stokes PL is not only of high scientific interest, but may also be applicable for, e.g., frequency conversion of semiconductor laser emission, a general microscopic understanding of this effect is desirable.

In this paper, we present low-temperature PL studies on CdTe/(Cd,Mg)Te multiple quantum-well (MQW) structures. We find efficient anti-Stokes PL from the barrier when the excitation energy is tuned to energies equal to or higher than the spectral position of the lowest heavy-hole excitonic $n=1$ QW transition, indicating a transfer of excitons from confined QW states to above-barrier states. At very low excitation densities this anti-Stokes PL exhibits a quadratic dependence on excitation intensity, changing into a linear dependence at higher intensities. These results are in full agreement with the assumption of a direct zero-phonon TSA process, if we assume that localized QW states and/or impurity bound QW states act as intermediate states. Time-resolved PL (TRPL) experiments show, in addition, that the photons necessary for the second absorption step can be provided by photon recycling, i.e., by the radiative recombination of QW excitons.

We have investigated a set of nominally undoped $CdTe/Cd_{0.6}Mg_{0.40}Te$ MQW structures grown by molecular beam epitaxy on (100)-oriented CdTe or $Cd_xZn_{1-x}Te$ substrates (for growth details, see Ref. 16). The samples consist of 7.5 nm thick wells separated by barriers with thicknesses of L_B = 144 nm, 77 nm (each consisting of 10 periods), and 7.5 nm (consisting of 75 periods). All structures exhibit disorder due to fluctuations of the QW width and as a consequence display inhomogeneous broadening of the excitonic resonances on the order of 2–4 meV [cf. Fig. 1(c)]. PL experiments are performed either using a synchronously pumped 76 MHz mode-locked dye laser (7 ps pulses) or using a frequency doubled 76 MHz Ti:sapphire laser ($\approx$140 fs pulses). In the time-integrated PL experiments, the luminescence is monitored by a photomultiplier or by a diode array. The streak camera technique with a time resolution of about 30 ps is applied for the time-resolved detection of the PL. All measurements are performed at 10 K and all anti-Stokes luminescence spectra are obtained using single laser beam excitation.

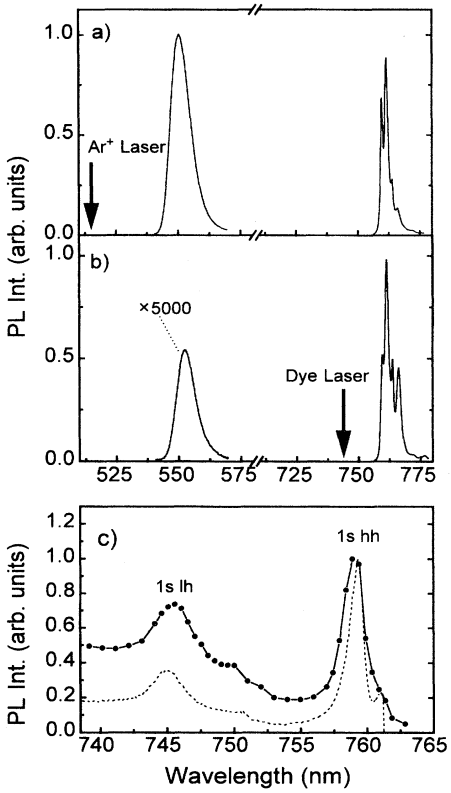

FIG. 1. (a),(b) Time-integrated PL spectra of the MQW with a barrier thickness of L_B = 144 nm at 10 K (a) excited above the barrier and (b) below the barrier. (c) Corresponding QW PLE spectrum (dashed curve) and anti-Stokes barrier PLE spectrum (solid curve) (both normalized to the respective maximum intensity at the 1s heavy-hole exciton resonance).

Figure 1 shows typical PL spectra of the MQW with L_B = 144 nm for excitation above (a) and below (b) the band gap of the barrier. In Fig. 1(a), the broad emission peak at approximately 560 nm is due to recombination in the barrier, whereas the structured PL at ≈760 nm is partly due to excitonic recombination in the QW's (two dominant high-energy peaks) and partly to substrate luminescence (two minor low-energy peaks together with the tail at even longer wavelengths). While showing a Stokes shift of 0.8 meV with regard to the 1s heavy-hole resonance in the PL excitation (PLE) spectrum [Fig. 1(c)], the high-energy peak of the QW PL is due to the recombination of localized excitons. The second peak of the QW PL can be assigned to bound excitons.[17,18] The overall intensity of the QW PL is comparable to that of the barrier, indicating efficient trapping of carriers from the barrier into the QW.[19] A very similar QW PL spectrum is observed if the MQW is excited below the band gap of the barrier [Fig. 1(b)]. Surprisingly, however, even under this excitation condition barrier luminescence can be observed, now occurring on the anti-Stokes side of the excitation. The efficiency of this anti-Stokes PL, given by the ratio of the spectrally integrated intensities of the barrier PL excited above and below the band gap of the barrier, is of the order of 0.1%. This anti-Stokes PL can be observed by the naked eye down to excitation powers of 50 μW focused to a spot size of ≈100 μm in diameter. We find similar results

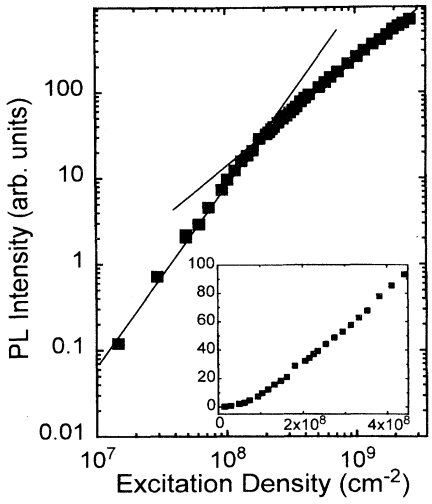

FIG. 2. Double-logarithmic plot of the density dependence of the anti-Stokes PL at 10 K. Linear regressions yield slopes of 2.1 and 1.08 for densities below and above 2×10^8 cm^{-2}, respectively. The inset shows a linear plot for low excitation densities.

for the MQW with L_B=77 nm; however, the intensity of the anti-Stokes PL is lower than in the case of L_B = 144 nm. This less efficient anti-Stokes PL is a consequence of more efficient carrier trapping in structures with thinner barriers.[20] In accordance with this explanation we do not find any anti-Stokes PL for the MQW with the thinnest barriers of L_B = 7.5 nm.

The dependence of the anti-Stokes PL on excitation energy, i.e., the PLE spectrum detected in the spectral region of the barrier PL, is shown as the solid curve in Fig. 1(c) together with the PLE spectrum of the QW (detected at 764 nm, dashed curve). Both PLE spectra reveal the n=1, 1s heavy-hole (hh) and light-hole (lh) exciton resonances at 759.4 nm and 745 nm, respectively. From these PLE results we conclude that the excitation scenario of the anti-Stokes barrier PL must involve QW states, since (i) the excitation spectrum of the anti-Stokes PL exposes the same features as the excitation spectrum of the QW PL and (ii) no anti-Stokes barrier luminescence is detectable for excitation energies less than the n=1 hh exciton resonance.

The spectrally integrated anti-Stokes barrier PL versus excitation density is shown for resonant excitation of the 1s hh QW exciton in Fig. 2 (L_B = 144 nm). The density dependence reveals two straight lines having slopes of 2.1 and 1.08 for densities below and above 2×10^8 cm^{-2}, respectively. This characteristic behavior can also be seen in the linear plot shown as an inset in Fig. 2. Virtually the same intensity dependence has been observed for the MQW with L_B=77 nm. For this sample the change in the slope occurs at ≈2.3×10^8 cm^{-2}. In this density regime both the QW and barrier PL (under direct excitation) exhibit linear dependences on excitation density. Hence, the data shown in Fig. 2 displays the intrinsic intensity dependence of the anti-Stokes process and is not related to a saturation of nonradiative traps in the QW or barrier.

On the basis of these experimental findings we now discuss the excitation mechanism leading to the anti-Stokes barrier PL. Since all experiments have been performed at 10 K,

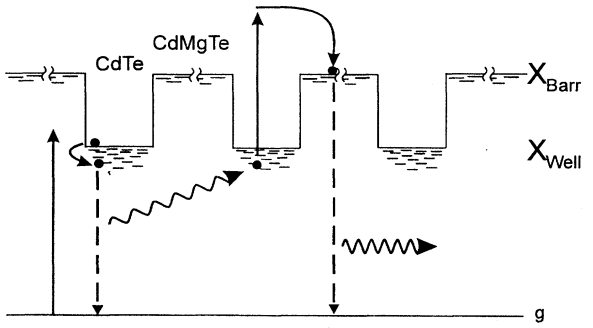

FIG. 3. Schematic illustration of the excitation scenario underlying the observed anti-Stokes photoluminescence. The horizontal solid lines represent the lowest exciton states in the barrier (X_{Barr}), the lowest, confined exciton states in the quantum well (X_{Well}), and the crystal ground state (g). Short horizontal lines indicate the presence of localized exciton states.

thermal activation over the barrier can be excluded, since the thermal energy $kT=0.9$ meV is much less than the energetic spacing between the lowest $n=1$ QW level and the band gap of the barrier, which is $\approx$420 meV in the conduction band and $\approx$180 meV in the valence band.[21] Furthermore, both TPA and Auger recombination can be ruled out, since they would exhibit a quadratic or cubic dependence on excitation density, respectively (for the entire intensity regime).

In the following we show that a TSA excitation process via localized exciton states or via excitons bound to impurities is the only possible explanation consistent with all the experimental data. The excitation scenario starts with the creation of electron-hole pairs in the QW as schematically illustrated on the left side of Fig. 3. After this initial excitation step electron-hole pairs relax to form excitons, which themselves relax down to localized and impurity bound states and establish a quasiequilibrium distribution. At low temperature these lowest, localized or impurity bound exciton states are populated, if the relaxation is efficient enough as compared to the optical lifetime to guarantee a perfect quasiequilibrium distribution. Increasing the excitation intensity, i.e., increasing the overall exciton density, means that higher-energy, less localized states become more and more populated, i.e., the populations of deeply localized states and of impurity states saturate. Since deeply localized QW states and impurity states have a very limited spatial extension, their corresponding center-of-mass wave function has contributions from all k states in the Brillouin zone. Accordingly, direct photon absorption out of deeply localized and impurity bound exciton states to high-energetic electron-hole pair states with a well-defined wave vector $\vec{k}$ should be possible without phonon participation, as illustrated in the middle part of Fig. 3. This second excitation process creates excitons (electron-hole pairs) with an energy higher than the band gap of the barrier, which then relax in energy and either reach the lowest barrier states or are trapped by the QW. Those carriers which reach the lowest barrier states relax down to localized exciton states of the ternary barrier material and then recombine radiatively giving rise to the observed anti-Stokes PL.

The excitation scenario illustrated in Fig. 3 consistently explains our observations, namely, the energy and density dependences of the anti-Stokes PL. The barrier PLE spectrum basically follows the QW PLE spectrum [Fig. 1(c)], i.e., the QW absorption profile, since in this TSA process localized or bound exciton states in the well represent the intermediate states (after relaxation). Within this TSA model, the intensity I_{AS} of the anti-Stokes PL is proportional (i) to the number of photons responsible for the second absorption step and (ii) to the population N_{exc} of the intermediate states, i.e., of the deeply localized and impurity bound exciton states. As will be shown, the number of photons inducing the second absorption step (N_{ph}) is directly proportional to the excitation laser intensity I. At low excitation intensities, i.e., in a regime where the population N_{exc} of deeply localized and impurity bound states is not saturated and thus is proportional to the excitation laser intensity I, the anti-Stokes PL I_{AS} is proportional to $N_{ph}N_{exc}$ and hence to I^2, as observed in Fig. 2 for excitation densities below 2×10^8 cm^{-2}. At higher intensities, when the populations of deeply localized and of impurity bound states saturate ($N_{exc}=N_{sat}$), the intensity I_{AS} of the anti-Stokes PL is proportional to $N_{ph}N_{sat}$ and therefore to I as observed in Fig. 2 for excitation densities greater than 2×10^8 cm^{-2}. Consequently, the change of the slope of the density dependence marks the density N_{loc} of deeply localized and impurity bound exciton states, i.e., $N_{loc}=2\times10^8$ cm^{-2} for the MQW with $L_B=144$ nm and $N_{loc}=2.3\times10^8$ cm^{-2} for the sample with $L_B=77$ nm. However, since there is no abrupt transition between deeply localized states composed of a broad spectrum of k states and shallow states having only center-of-mass wave vectors adjacent to the Γ point, the density N_{loc} has to be interpreted as a complicated average value.

In principle, the second absorption step can also be of indirect character, i.e., any localized *and* delocalized QW excitons are further excited by a phonon-assisted absorption process. However, this would result in a quadratic dependence of the anti-Stokes PL on laser intensity (over the entire range), since the intermediate states would not saturate. In other words, a purely phonon-assisted absorption process cannot account for the transition from the quadratic to the linear intensity dependence, and thus cannot be the dominant excitation process.

The above-mentioned PL and PLE experiments [except the "conventional" one of Fig. 1(c)] have all been performed using the synchronously pumped 76 MHz mode-locked dye-laser system generating 7 ps pulses. If we assume that the photons inducing the second absorption step are laser photons, the entire excitation scenario for the anti-Stokes PL illustrated in Fig. 3 should be completed within 7 ps.[22] However, within 7 ps the relaxation down to deeply localized or impurity bound states is certainly not completed.[23,24] Furthermore, considering the relatively high efficiency of the anti-Stokes PL it seems unlikely that in these pulsed experiments the photons inducing the second absorption step are only laser photons. The following time-resolved PL experiments show indeed that the second absorption step is mainly induced by photons provided by photon recycling, i.e., the photons stem from radiative recombination processes of QW excitons. Figure 4 shows the transients of the QW PL excited at the $n=1$ lh excitonic resonance (solid curve), and of the spectrally integrated barrier PL for above- (dashed curve) and below-barrier excitation (dotted curve), respectively. The intensity of the QW PL decays monoexponentially over

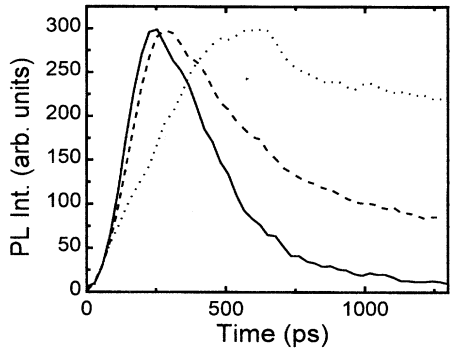

FIG. 4. Time-resolved PL spectra of the MQW sample with $L_B = 144$ nm; solid curve: QW PL; dashed curve: barrier PL excited by a frequency doubled Ti:sapphire laser at ≈ 400 nm; dotted curve: anti-Stokes barrier PL excited at the lowest hh exciton resonance of the QW. All spectra are normalized.

nearly two orders of magnitude with a time constant of 230 ps, a typical value for exciton recombination in II-VI QW's.[25] The barrier PL for above-barrier excitation exhibits a decay constant of 650 ps, which is in reasonable agreement with measurements on $Cd_xMn_{1-x}Te$ epilayers with a similar composition.[26] The rise times of both QW and barrier PL transients are comparable and are determined by exciton formation and relaxation within localized states. The anti-Stokes barrier PL also decays with a time constant of 750 ps, whereas its rise time of 210 ps is much longer than that of the barrier PL for above-barrier excitation. Obviously, the rise time of the anti-Stokes PL is similar to the decay time of the QW PL. We conclude that this delayed rise reflects the dynamics of the generation process of above-barrier excitons (electron-hole pairs). The photons inducing the "above-barrier excitation" of deeply localized and impurity bound QW excitons stem from the excitonic QW PL as schematically illustrated in Fig. 3. In other words, the second photon for the two-step absorption process is provided by photon recycling.[27,28] We note that the anti-Stokes barrier PL also occurs for continuous wave excitation, under which the second excitation step should be induced by both QW PL photons and laser photons.

Finally, we would like to note that the observed anti-Stokes transfer of excitons is a general feature of semiconductor heterostructures that display disorder. Accordingly, we have recently observed low-temperature anti-Stokes PL also for other QW structures, e.g., $CdTe/Cd_xMg_{1-x}Te$ and $GaAs/Al_xGa_{1-x}As$ asymmetric double quantum wells (ADQW's).[29] Since retrapping is a competing process for the anti-Stokes barrier PL, specially designed barrier structures which prevent carriers from being retrapped into the QW's should lead to even more intense anti-Stokes PL. Altogether, the detailed knowledge of the microscopic mechanism for this anti-Stokes PL in semiconductor heterostructures could probably lead to important novel concepts for light-emitting devices.

In summary, we have presented detailed experimental studies of anti-Stokes barrier PL occuring in $CdTe/Cd_xMg_{1-x}Te$ MQW structures. This anti-Stokes PL is caused by a two-step absorption process involving deeply localized or impurity bound exciton states in the quantum wells. We have shown that the photons for the second absorption step can be provided by photon recycling of exciton recombination in the quantum well.

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