Photoluminescence Up-Conversion Induced by Intersubband Absorption in Asymmetric Coupled Quantum Wells

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We report a new mechanism of photoluminescence up-conversion in undoped GaAs-AlGaAs asymmetric coupled quantum wells. Under band-to-band excitation, resonant excitation of the $E_1 \rightarrow E_2$ intersubband transition is shown to result in a finite nonthermal occupation of the E_2 subband, giving rise to an $E_2 \rightarrow HH_1$ photoluminescence. The induced luminescence closely follows the polarization selection rules and the spectral dependence of the intersubband absorption. We show that this up-conversion scheme can be used to estimate the intersubband scattering time, which is found to be 2.5 ± 0.7 ps.

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Band-to-band photoluminescence (PL) from higher conduction subbands in undoped semiconductor multiple quantum wells (MQW) is usually difficult to observe, since the electron scattering time to the ground conduction subband is much shorter than the band-to-band recombination time. Nonthermal occupation of higher subbands can be provided by sequential resonant tunneling of the electrons in the MQW structure under application of an electric field perpendicular to the layers. The application of a perpendicular electric field was demonstrated to induce an interband luminescence from the second and third electronic subbands in undoped superlattices [1]. It was also shown that an intersubband emission can take place [2]. For this type of experiment, the lifetime of the electrons in the excited subbands is of critical importance. It is now well established that the intersubband relaxation of the electrons is dominated by the emission of optical phonons when the energy separation between the subbands is larger than the longitudinal-optical (LO) phonon energy [3]. However, the value of the intersubband scattering time is controversial, since the experimental values range from a few hundreds of femtoseconds to a few picoseconds [1-7]. Recent theoretical calculations of two-dimensional electron-LO-phonon scattering rates give values on the order of 1 ps or less for wells with infinite potential barriers, although some variation is predicted with the well width, the finite barrier potential, and the respective localization of the envelope wave functions of the initial and final subbands [8-10].

In this Letter, we report the first observation of interband photoluminescence from the second electronic subband to the first heavy-hole subband ($E_2 \rightarrow HH_1$) induced by an intersubband absorption from the first to the second electronic subband ($E_1 \rightarrow E_2$) in undoped GaAs-AlGaAs asymmetric coupled quantum wells (ACQW). The intersubband excitation is shown to result in a nonthermal occupation of the E_2 subband. The induced luminescence closely follows the polarization selection rules and the spectral dependence of the intersubband absorption. As in Ref. [1] the ratio of population between the second and first subbands deduced from the corresponding PL intensities provides an estimate of the intersubband scattering time τ_{21} without requiring subpicosecond time-resolution techniques. Since the absorption of photons at mid-infrared energies (MIR, 0.11-0.14 eV) translates into the emission of near-visible photons (1.758 eV), this mechanism may be seen as an up-conversion process.

Since the $E_2 \rightarrow HH_1$ transition is forbidden in symmetric quantum wells, we used an asymmetric MQW structure. The ACQW structure, shown in the inset of Fig. 1, is designed to optimize the overlap of the envelope wave functions between subbands E_2 and HH_1 and to

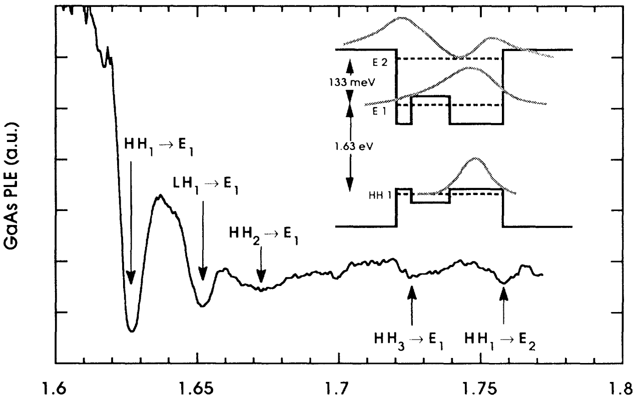

FIG. 1. Photoluminescence excitation spectrum of the substrate GaAs luminescence. The spectrum may be seen as a transmission spectrum of the asymmetric coupled quantum wells. The identified interband transitions are indicated by arrows.

present an intersubband resonance $E_1 \rightarrow E_2$ at a photon energy compatible with excitation by a cw CO_2 laser. The nonintentionally doped 100-period ACQW structure is grown by molecular beam epitaxy on a semi-insulating GaAs substrate. Each period, sandwiched between 10.0 nm thick $Al_{0.3}Ga_{0.7}As$ barriers, consists of a 0.85 nm thick GaAs well followed by a 2.4 nm thick $Al_{0.14}Ga_{0.86}As$ barrier and by a 3.7 nm thick GaAs well. The wafer is cleaved in 1.0 mm long samples. The sample facets are then polished at a 45° angle. Experiments are carried out at 77 K. The polarized MIR beam is focused at normal incidence on the sample facets and undergoes two total internal reflections in the sample. This configuration allows a double pass within the MQW layer along with a large coupling of the p-polarized MIR radiation to the intersubband transition [11]. The near-infrared pump beam from a tunable cw Ti:sapphire laser (1.58–1.78 eV) is focused at a 45° angle onto the sample surface. The luminescence focused on the entrance slit of a 0.64 m monochromator is detected using a low-noise Si photodiode.

Preliminary experiments are concerned with spectroscopic measurements to assess the energy position of both the interband and intersubband transitions. Standard photoluminescence spectroscopy under excitation by an Ar^{++} laser reveals an excitonic $HH_1 \rightarrow E_1$ resonance at 1.63 eV along with luminescence at 1.51 eV originating from the GaAs substrate. Figure 1 shows an excitation spectrum of the 1.51 eV GaAs photoluminescence which reflects the transmission of the ACQW layer provided that the MQW PL intensity absorbed in the GaAs substrate is weaker than the transmitted pump intensity, which is the case for not too absorbing MQW layers. As seen in Fig. 1, the $HH_1 \rightarrow E_2$ excitonic transition is found to occur at 1.758 eV. We have also performed photoinduced intersubband spectroscopy [12] with the pump laser set at 1.675 eV by varying CO_2 laser wavelength. Experiments of this type are described in detail in a previous paper [13]. Under p-polarized MIR excitation, the intersubband $E_1 \rightarrow E_2$ resonance is found at 133 meV with a full width at half maximum of 7 meV. The intersubband resonance vanishes when the MIR polarization is rotated parallel to the layers, as expected from the selection rules associated with transitions between conduction subbands [14].

For the next series of results the intersubband excitation photon energy is set at 133 meV and the MIR beam is p polarized. Figure 2 shows the influence of the intersubband excitation on the PL spectra around the $HH_1 \rightarrow E_2$ energy. The bottom curve is the spectrum without intersubband excitation while the upper spectra correspond to increasing MIR intensities. The pump excitation is at 1.675 eV, i.e., electrons are excited well below the second conduction subband. Two main features which are not present on the spectrum without intersubband excitation can be noticed. By comparison with the transmission spectrum of Fig. 1, the strongest peak at 1.758 eV is due to the $E_2 \rightarrow HH_1$ luminescence while the smaller and somewhat broader peak at 1.725 eV is attributed to the $E_1 \rightarrow HH_3$ luminescence. Their amplitudes grow with increasing intersubband excitation intensities. Both peaks vanish when the intersubband excitation is polarized in the plane of the layers. The occupation of the E_2 and HH_3 subbands is thus clearly related to the presence of the intersubband excitation, although one cannot exclude at this step a thermal population of both subbands.

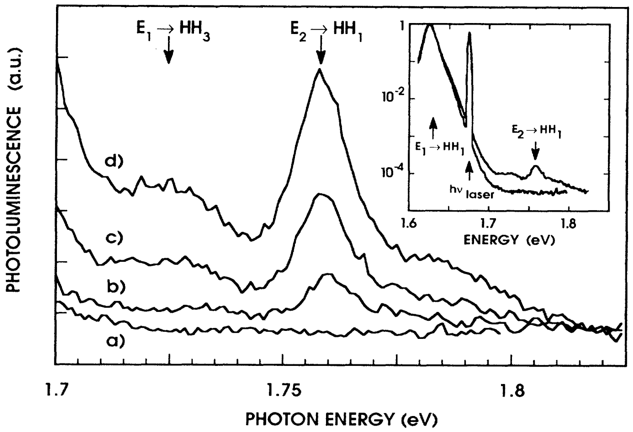

FIG. 2. Photoluminescence spectrum around the $E_2 \rightarrow HH_1$ energy for four intersubband intensities: (a) without intersubband excitation, (b) $I_{exc} = 3.6$ kW cm^{-2}, (c) $I_{exc} = 7.0$ kW cm^{-2}, and (d) $I_{exc} = 15.9$ kW cm^{-2}. The interband excitation is set at 1.67 eV with an intensity of 29 W cm^{-2}. The inset shows the whole PL spectrum in logarithmic scale without intersubband excitation (lower curve) and for $I_{exc} = 7.0$ kW cm^{-2} (upper curve).

The inset of Fig. 2 shows the whole PL spectrum with and without intersubband excitation. As revealed by the exponential decrease of the high-energy side of the PL from the first conduction subband, the carrier temperature increases in the presence of intersubband excitation. However, the carrier temperature for the most intense excitation is deduced to be ≈ 110 K, which is too small to induce a significant occupation of the second conduction subband. Therefore, these results give a first demonstration that the induced luminescence at 1.758 eV is due to a nonthermal occupation of the second subband via intersubband absorption. A similar absorption mechanism between the valence subbands HH_1 and HH_3 could be invoked to explain the existence of the induced $E_1 \rightarrow HH_3$ luminescence. However, this process is unlikely, since the intersubband transition $HH_1 \rightarrow HH_3$ would be detuned by 20–40 meV from the excitation energy, based on the estimated difference between the $HH_3 \rightarrow E_1$ and $HH_1 \rightarrow E_1$ transition energies deduced from the transmission spectrum. We believe that the occupation of the HH_3 subband results from the reabsorption of the E_2

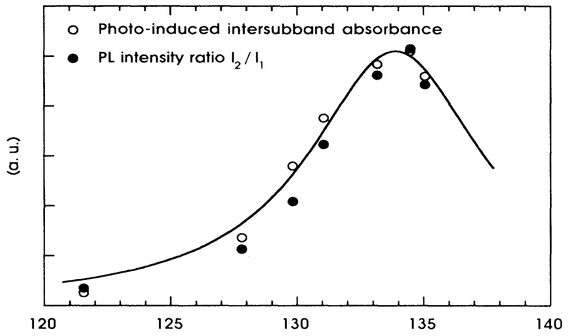

FIG. 3. Photoinduced intersubband absorbance (open circles) and photoluminescence intensity ratio I_2/I_1 (full circles) vs the photon energy of the intersubband excitation. The solid curve is a Lorentzian fit.

$\rightarrow HH_1$ luminescence.

Further evidence of the close relationship between the induced $E_2 \rightarrow HH_1$ luminescence and the intersubband excitation is illustrated in Fig. 3, which shows the corresponding PL intensity versus the MIR photon energy for a p polarization of the MIR beam. For comparison purposes, the photoinduced intersubband absorbance measurements are also reported in the figure. As seen, the evolution is almost identical within experimental accuracy for the induced luminescence and the intersubband absorbance. As for the intersubband absorption, no resonance for the induced luminescence is observed when the MIR excitation is s polarized.

Further evidence of the nonthermal occupation of the second conduction subband induced by the intersubband absorption process is shown in Fig. 4, which plots the intensity ratio I_2/I_1 between the induced $E_2 \rightarrow HH_1$ PL and the $E_1 \rightarrow HH_1$ PL versus the effective intersubband excitation intensity in the sample for a p-polarized excitation. The band-to-band excitation is at 1.675 eV with a low incident power density of 29 W/cm^2, resulting in an estimated carrier density in the first conduction subband ranging from 6.8×10^8 cm^{-2} for the surface quantum well to 3.2×10^8 cm^{-2} for the deeper well [15]. As seen in Fig. 4, the PL intensity ratio increases almost linearly in the investigated range of intersubband excitation power densities. The signature of a thermal occupation of the second conduction subband would appear as a fast exponential-like growth of the PL intensity ratio with the excitation intensity, which is not experimentally observed. Similarly, a linear increase with excitation power density is also observed for the intensity ratio between the $E_1 \rightarrow HH_3$ PL and $E_1 \rightarrow HH_1$ PL which is consistent with a nonthermal occupation of the third heavy-hole subband due to the reabsorption effect previously invoked.

The observed up-conversion process from the MIR 0.133 eV radiation to the near-visible 1.758 eV radiation is thus clearly related to a linear population transfer from the first to the second conduction subband. Although one cannot exclude some contribution from two-photon nonlinear processes, the induced PL intensity would be strongly dependent on the band-to-band excitation photon energy, which is not the case since the experimental results are well reproduced using band-to-band excitation by a visible argon laser. Finally, note that in Fig. 4 the intensity ratio, which reflects the yield of the up-conversion process, reaches values of the order of 10^{-3}, which are easily detectable without requiring photon-counting techniques.

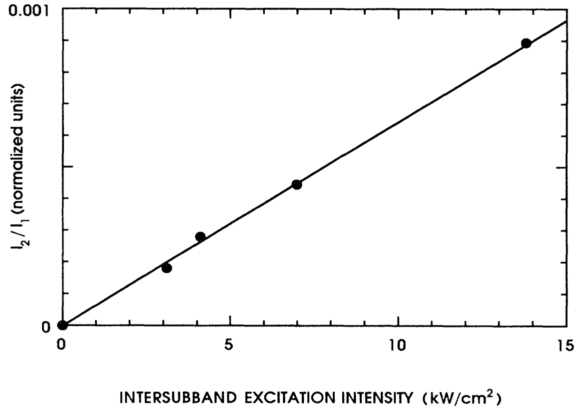

FIG. 4. Luminescence intensity ratio I_2/I_1 vs intersubband excitation intensity. The intersubband excitation is set at resonance. The interband excitation is at 1.67 eV with an intensity of 29 W cm^{-2}.

The PL intensity ratio I_2/I_1 under cw excitation is directly related to the occupation of the first and second conduction subbands and to the oscillator strength of each band-to-band transition [1]. For a single quantum well, this ratio can be expressed as

$$\frac{I_2}{I_1} = \frac{n_2}{n_1}\frac{f_2}{f_1}, \tag{1}$$

where n_1 and n_2 represent the occupation factors of the first and second conduction subbands, respectively, and f_2/f_1 is the ratio of the oscillator strengths associated with the E_2-HH_1 and E_1-HH_1 transitions, respectively, which can be calculated using the envelope function formalism to be ≈ 0.024 [16,17]. Since the band-to-band relaxation times are known to be much longer than the intersubband scattering time, the occupation ratio can be easily determined by considering only the two conduction subbands:

$$\frac{n_2}{n_1} \approx \tau_{21}\frac{\sigma_{12} I_{\text{exc}}}{h\nu_{\text{exc}}}, \tag{2}$$

where $h\nu_{\text{exc}}$ and I_{exc} are, respectively, the photon energy and the intensity of the intersubband excitation, and σ_{12} is the absorption cross section associated with the intersubband transition. The value of σ_{12} deduced from the photoinduced intersubband absorption measurements is

$\approx 1.2\times10^{-14}$ cm^2, in good agreement with calculations [18]. The validity of Eq. (2) is restricted to mid-infrared intensities below the saturation level of the intersubband absorption. This last condition is fulfilled in our experiments [19]. As seen from Eqs. (1) and (2), a linear increase is predicted for the PL intensity ratio with the intersubband excitation intensity in agreement with measurements.

Equations (1) and (2) hold for each quantum well within the MQW layer. However, because of the pump and MIR attenuation and of the luminescence reabsorption in the MQW layer, propagation effects must be taken into account for estimating the actual intensity ratio of the luminescence radiations exiting from the sample [20]. By doing this and by using the experimental value of I_2/I_1, we deduce an intersubband scattering time τ_{12} of 2.5 ± 0.7 ps instead of 2.2 ps with Eqs. (1) and (2). Note that this value of τ_{12} is slightly longer than previously reported scattering times for undoped symmetric quantum well structures [1,7]. Although detailed calculations of the electron-phonon interaction are beyond the scope of this paper, one expects that the relaxation of electrons from the higher subband through emission of bulklike slab LO phonons would be slower in our structure than in a symmetric quantum well. Indeed, since the slab phonon modes have nodes at each interface, the electron-phonon interaction in our ACQW structure would correspond in a symmetric quantum well to high-order mode interactions, which are generally weaker than the lower mode interactions [9]. However, the role of interface phonon modes in the relaxation process may be enhanced in the ACQW structure because of the presence of four interfaces. Our τ_{12} value is in close agreement with previously reported measurements on ACQW structures using subpicosecond time-resolved luminescence techniques [21].

The efficiency of the up-conversion process from the MIR 0.133 eV radiation to the near-visible 1.758 eV radiation is directly related to the product of the intersubband absorption cross section and the intersubband scattering time. An increase of the efficiency by more than 1 order of magnitude is then expected if the intersubband relaxation only involves acoustic phonons [3,21]. This condition could be fulfilled by a proper design of the ACQW structure in order to obtain an intersubband resonance at an energy inferior to the LO-phonon energy.

In summary, we have shown that an up-converted photoluminescence from the second electronic subband to the first heavy-hole subband can be induced by an intersubband absorption from the first to the second electronic subband in undoped GaAs-AlGaAs asymmetric coupled quantum wells. Results demonstrate that a nonthermal occupation of the E_2 subband can be achieved using this resonant intersubband excitation. The occupation ratio between the second and first subbands is deduced from the corresponding PL intensities in order to estimate the intersubband scattering time τ_{21}, which is found to be 2.5 ± 0.7 ps.

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[20] The pump intensity and the carrier density n_1 in each ACQW is calculated as indicated in Ref. [15]. The intersubband absorbance $\exp(-\sigma_{12}n_1)$ is then computed, allowing $I_{\rm exc}$ to be estimated in each well. We next assume I_1 to be proportional to the band-to-band excitation intensity, which is experimentally verified. For each ACQW, I_2 is calculated using Eqs. (1) and (2). Both I_1 and I_2 are multiplied by $\exp(-mA)$ to account for the reabsorption in the m upper ACQWs, with $A=7.4\times10^{-3}$ (6×10^{-3}) at E_2-HH_1 (E_1-HH_1) photon energy [16]. I_1 and I_2 are then summed over the pump and MIR propagation path, respectively, to calculate the ratio of exiting luminescence intensities.

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