High-Efficiency Energy Up-Conversion by an "Auger Fountain" at an InP-AlInAs Type-II Heterojunction

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(Received 28 February 1994)

Luminescence of bulk InP at 1.41 eV is observed when photoexciting a type-II InP-AlInAs single heterojunction above the spatially indirect band gap at 1.23 eV. This energy up-conversion effect, which is extremely efficient even at moderate pump power, is due to an "Auger fountain" mechanism producing high energy holes which redistribute over the heterostructure and recombine with native electrons in the InP layer. The analysis of this phenomenon suggests technological applications as well as analogies with other fields like photochemistry.

PACS numbers: 73.20.Dx, 42.65.Ky, 78.66.Fd

Photon energy up-conversion, like perpetual motion, seems to be a challenge to thermodynamics. Most energy up-conversion effects, like the anti-Stokes lines in Raman spectroscopy, rely on the existence of a hot reservoir, for instance, thermal population of the phonon modes, and the amount of energy which can be up-converted is of the order of kT. Another example is nuclear fusion, which requires very hot plasmas to overcome the Coulomb potential barrier. "Cold" processes do exist, like second harmonic generation or two-photon sequential absorption [1] in nonlinear optics, but they are usually quite unefficient at the moderate pump power found in a cw experiment. In this Letter, we report on an energy up-conversion effect which is both cold and astonishingly efficient under cw excitation conditions usual in semiconductor physics. Paradoxically, this effect is linked to Auger recombination, which is better known as a nonradiative process and a fundamental limitation to the efficiency of semiconductor lasers [2]. The "Auger fountain" works in the following way: An Auger recombination event involving one electron and two holes leaves a high energy hole, which, during thermalization, is redistributed in k space (e.g., a different band) or in real space [3] (e.g., a different part of the sample). If the final state is metastable enough, this hole is available for a radiative recombination at an energy possibly higher than the pump energy. A very weak luminescence from the spin-orbit split-off band has indeed been observed in the past in bulk GaSb [4] and attributed to such a mechanism. Luminescence up-conversion due to inter-Landau level excitations by the Auger process in a doped quantum well has also been reported [5]. As we evidence below, the restricted conditions for a high efficiency can be found in a type-II heterostructure where the heterojunction electric field drifts the Auger hole into the "barrier" material and avoids its thermalization in the fundamental level. Type-II heterostructures offer a completely original situation with respect to radiative as well as Auger recombinations, since electrons and holes are spatially separated and recombination is allowed only by the small overlap of the wave function tails outside the potential wells where they are localized. Recently, we started the investigation of InP-AlInAs heterostructures, which are the most regular among the type-II systems fabricated so far, with electrons localized in InP and holes in AlInAs. This study revealed several interesting features, like the noncommutativity of band discontinuities [6] or an unexpected low threshold laser emission [7]. Here, we report on luminescence energy up-conversion by the Auger fountain mechanism in a InP-AlInAs single heterojunction [8].

Our sample was grown by metal-organic chemical vapor deposition on a n-doped InP substrate. As shown in Fig. 1(a), this heterostructure simply consists of a 1000 Å thick InP buffer layer, with a low n-type residual doping in the 10^{14} cm^{-3} range, followed by a 1000 Å thick AlInAs layer with a n-type residual doping in the 10^{16} cm^{-3} range. The free surface is protected by a 50 Å InGaAs layer. Calculation of the charge transfer at the interface [9] for a conduction band offset equal to 470 meV [6] and an AlInAs doping level $N_D = 2 \times 10^{16}$ cm^{-3} yields a two-dimensional electron gas (TDEG) with an areal density $n_S = 3 \times 10^{11}$ cm^{-2}. The electric field at the interface is 30 kV/cm. Electron and heavy hole confinement energies in their respective quasitriangular quantum wells are 30 and 20 meV, respectively. The low temperature photoluminescence (PL) spectrum under low power excitation by a He-Ne laser is shown in Fig. 1(b). A strong line "A" corresponding to recombination at the type-II interface is observed at 1.23 eV. The PL from the InP buffer layer shows up as a sharp line "B" at 1.41 eV, emerging from a broad background "C" due to the substrate. A weaker PL line "D" from the AlInAs layer appears at 1.63 eV, which corresponds to a 4% Al-rich composition with respect to the alloy lattice matched to InP. Photoluminescence excitation (PLE) spectra [10] of these lines [dashed lines in Fig. 1(b)] directly show the corresponding absorption gaps. It is remarkable that the gap associated with the interface can be observed directly from the excitation spectrum of the A line in spite of the

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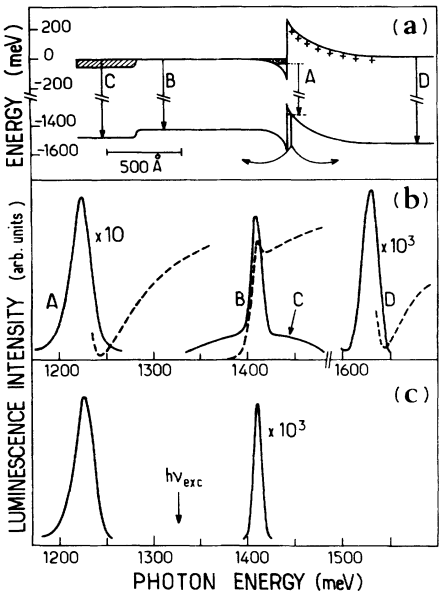

FIG. 1. (a) Sketch of the band structure of the InP-AlInAs heterojunction. (b) Luminescence spectrum (solid lines) under low power excitation with an He-Ne laser and excitation spectra (dashed lines) of the various lines [10]. (c) Luminescence spectrum with a 20 mW excitation power at $h\nu_2 = 1.325$ eV, showing the up-converted InP luminescence.

very small absorption associated with the type-II single heterojunction.

We now discuss results obtained using a Ti:sapphire tunable laser with a power of a few tens of mW and loosely focused on the sample using a long focal ($f = 0.8$ m) lens, which gives a beam waist of 1 mm. For an excitation energy above the InP band gap ($h\nu_1 = 1.51$ eV), the PL spectrum shows very little dependence on the excitation power: the line shapes do not change appreciably and, as shown in Fig. 2(a), the nearly identical integrated intensities of the A and B lines vary linearly with the pump power over several decades. This proves that the radiative efficiencies are essentially constant for this range of excitation densities. However, when the sample is excited at $h\nu_2 = 1.325$ eV, i.e., between the interface and InP band gaps, a rather unusual feature is observed: as shown in Fig. 1(c), the luminescence from the InP buffer layer can still be observed, although much weaker than before. As can be seen on Fig. 2(b), this B line now has a quadratic dependence on the excitation power I, while the A line still shows the linear variation. As we ensured a perfect spectral filtering of the laser beam, this InP luminescence clearly corresponds to an up-conversion of the exciting photon energy. To discriminate between possible explanations like two-photon absorption, intraband absorption by photocarriers, etc., we have examined the wavelength dependence of the effect at a fixed pump intensity, which amounts to measuring an "anti-PLE" spectrum of an anti-Stokes PL line. We find that the signal varies exactly like

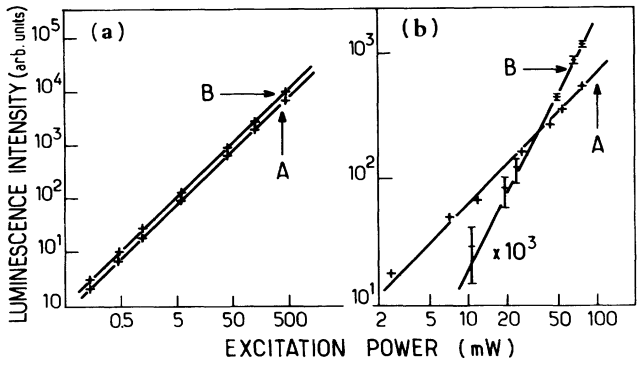

FIG. 2. Integrated intensities of the interface A and InP B luminescence lines versus the pump intensity (a) for an excitation energy $h\nu_1 = 1.51$ eV and (b) for an excitation at $h\nu_2 = 1.325$ eV.

the square of the interface absorption α^A determined by the normal PLE spectrum of the A line [Fig. 1(b)]. As in these experimental conditions the areal density of photocarriers is much lower than the TDEG density; this result proves that the up-converted signal is directly proportional to the photohole density p_S. The only mechanism which immediately explains both the $(I)^2$ and $(\alpha^A)^2$ dependences is the "fountain" effect due to the Auger process involving a native electron and two photoholes, as sketched in Fig. 1(a): those of the high energy Auger holes which fall toward the InP side are pushed away from the interface by the heterojunction electric field. They thermalize at the top of the InP valence band and recombine there with native electrons.

This effect is easily modeled using simple rate equations. With the superscripts A and B referring to the interface and InP luminescences and the subscripts 1 and 2 referring to the excitation energies 1.51 and 1.325 eV, we write four equations in the form

$$L^{A,B_{1,2}} = g\eta^{A,B}G^{A,B_{1,2}}, \tag{1}$$

where L is the signal intensity, G the corresponding generation rate, η the radiative efficiency, and g an external coupling constant. For photocarriers, we have

$$G_{\mathrm{ph}} = \alpha I(1 - R)/h\nu, \tag{2}$$

where α (dimensionless) is the related absorption (i.e., the fraction of incident photons absorbed by the corresponding transitions), $R \approx 0.3$ the sample reflectivity, and $h\nu$ is the exciting photon energy. For the Auger carriers fed to InP, we write in formal analogy with the bulk situation

$$G_{\mathrm{Auger}} = 0.5SC_p n_S p_S^2, \tag{3}$$

where S is the surface of the excited region. C_p is the two-dimensional equivalent of the usual Auger coefficient. The 0.5 factor accounts for the fact that only half of the Auger holes fall toward InP. As already mentioned, n_S is essentially equal to the density of native electrons

in the TDEG. Finally, if the radiative part of the interface recombination follows an exponential law with a time constant τ^A, we have (assuming that the Auger holes falling towards AlInAs are fed back to the interface)

$$d/dt\, Sp_S = G_{\rm ph} - Sp_S/\tau^A - 2G_{\rm Auger}. \quad (4)$$

Our investigations of the luminescence decay, using a cavity dumped Ar^+ laser at low power, yield $\tau^A = 15$ ns. As this value is comparable with the pulse duration, we cannot establish directly that the decay follows a simple exponential law, but this assumption is clearly supported by the observation of a linear kinetics under these excitation conditions.

As long as $G_{\rm Auger}$ remains negligible, this set of equations predicts the observed dependences of L^{A_1}, L^{B_1}, L^{A_2}, and L^{B_2} on the excitation intensity I and the related absorptions. Using $n_S = 3 \times 10^{11}$ cm^{-2}, $\alpha^{B_1} = 0.1$ for the absorption by the 1000 Å thick InP buffer layer, and $\alpha^{A_1}/\alpha^{A_2} = 5.5$ as measured directly on the extended PLE spectrum of the A line, the combination of the experimental data yields $C_p(\alpha^{A_2})^2 = 3.2 \times 10^{-20}$ cm^4 s^{-1}.

At this stage, further elucidation of the situation has to rely on a calculation of the interface absorption α^A. This is done by solving numerically the Schrödinger equation for the envelope functions in the potential sketched in the inset of Fig. 3, using a transfer matrix method. While the threshold absorption depends considerably on the actual parameters (electric field at the interface and depth of the triangular quantum well), we observe that, as a consequence of an effective sum rule, the calculated absorption at 1.32 eV, about 80 meV above the interface band gap, remains nearly constant and equal to 10^{-4}. However, this result can be changed considerably and in both directions by simulating equally plausible imperfections of the interface: by adding two monolayers of InAs at the interface, as suggested by the results of Brasil *et al.* [11], we get an absorption 10 times larger [spectrum (b) in Fig. 3], while by simulating a 30 Å wide graded interface, we get an absorption about 50% smaller [spectrum (c) in Fig. 3]. The strong absorption with a quasiparabolic profile above 1.42 eV corresponds to direct transitions in the 1000 Å thick InP layer forming the left part of the structure. It does not depend on the modeling of the interface potential and yields the expected value. Using $\alpha^{A_2} = 10^{-4}$ and the data for $I = 100$ mW at $h\nu_2$, we get $C_p = 3.2 \times 10^{-12}$ cm^4 s^{-1}, and $p_S = 6 \times 10^7$ cm^{-2}. Hence, p_S is always negligible compared to the density of native electrons, which explains why the luminescence line shape, line position, and lifetime are constant in our range of laser excitation.

To complete this study, we then investigate the saturation of the up-conversion effect by increasing the excitation density, using a tighter focusing ($f = 50$ mm) and a slightly shorter wavelength ($h\nu_3 = 1.375$ eV) where more power is available from the Ti:sapphire laser. The interface absorption at $h\nu_3$ is also somewhat larger, as $\alpha^{A_3}/\alpha^{A_2} = 1.33$. We show in Fig. 4 the ratio of the InP and interface luminescences L^{B_3}/L^{A_3} as a function of the laser intensity, together with fits using Eqs. (1)–(4). At "low" power, we find again the quadratic and linear dependences, which yield about the same value of $C_p(\alpha^A)^2$ as before. At higher excitation, the up-converted luminescence tends to become linear, and the interface luminescence saturates as $I^{1/2}$. This regime rather measures the value of $C_p(\alpha^A)^3$, hence we now have a complete solution, giving $C_p = 3.9 \times 10^{-12}$ cm^4 s^{-1} and $\alpha^{A_3} = 1.9 \times 10^{-4}$ (dotted line in Fig. 4) or $C_p = 4.6 \times 10^{-11}$ cm^4 s^{-1} and $\alpha^{A_3} = 0.73 \times 10^{-4}$ (dashed line in Fig. 4). The first set of values, which gives a better agreement with the loose focusing results, is clearly more satisfactory, as other saturation mechanisms (heating) can explain the deviation of

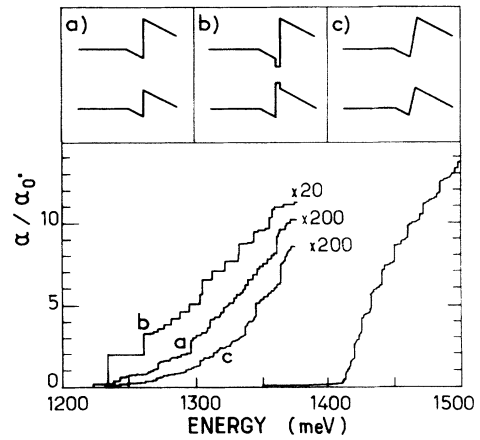

FIG. 3. Calculated absorption spectra using numerical solutions of the Schrödinger equation for the potentials sketched in the inset: ideal heterojunction (a), or heterojunction with an additional 5.6 Å InAs layer at the interface (b), or with a 30 Å wide graded interface (c). The constant $\alpha_0 = 6 \times 10^{-3}$ is the absorption by a heavy-hole to electron transition in a type-I QW.

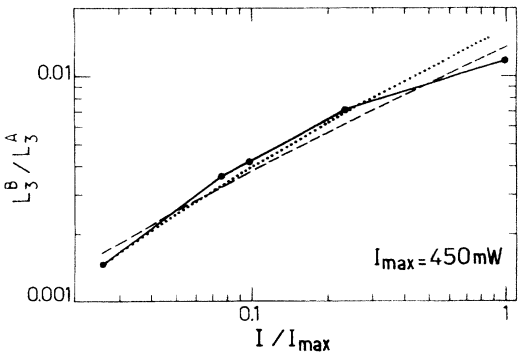

FIG. 4. Ratio of the InP to interface luminescence intensities as a function of the pump power at $h\nu_3 = 1.375$ eV, under "tight" focusing. The solid line is drawn through the data points and the dashed and dotted lines are fits using Eqs. (1)–(4) and slightly different fitting parameters.

the highest excitation data from our simple model. Given the simplicity of the model and the range of experimental data, the agreement is rather fair. The figure for α^A indicates a nearly ideal interface, which might be the strangest part of our results. Another surprise is the value of the Auger coefficient: A natural, although completely arbitrary scaling of the electron and hole densities by the extension of their wave functions along the z axis allows a reduction to an "equivalent three-dimensional Auger coefficient" which turns out to be about 3 orders of magnitude larger than the values usually reported for small spin-orbit bulk III-V semiconductors or type-I quantum wells [4,12,13]. This seems at odds with the observation of the fair laser effect in InP-AlInAs superlattices [6].

Finally, if we take into account the considerable difference between the interface and InP radiative efficiencies $\eta^A/\eta^B \approx 100$ (which is evidenced directly by the nearly equal luminescence intensities at $h\nu_1 = 1.51$ eV, in spite of the $\approx$1:100 absorption ratio), our high excitation data show that the up-conversion process reaches a nearly total efficiency (half of the pump photons up-converted) at an excitation density of the order of 10 kW/cm^2, which is an amazingly small intensity for nonlinear optics. This points to possible applications: By appropriate band gap engineering (e.g., by the deliberate addition of a thin InAs layer), it should be possible to lower the interface band gap down toward half the InP band gap and increase the energy conversion up to about 700 meV. As at the same time the interface absorption would increase, this might open interesting perspectives for infrared image conversion. Also, it is noteworthy that the main ingredient of this new Auger fountain effect, which is the spatial separation of the ground and excited states avoiding the thermalization of the Auger carriers, may be found in other systems like organic molecules. This suggests the possibility of analogous effects in photochemistry.

In conclusion, we have observed high efficiency photon energy up-conversion by an Auger fountain mechanism. Paradoxically, the efficiency of this huge optical nonlinearity is due to the importance of a nonradiative recombination path. This observation raises several questions concerning the role of Coulomb forces, k-conservation or nonconservation etc., for Auger or other many-particle interactions at type-II interfaces. It also opens unexpected application perspectives and suggests possible analogies in other fields.

We thank T. Lebihen and C. Delalande for their help and the use of their Ti:Sapphire laser and P. Roussignol for fruitful discussions. LPMC-ENS is UA No. 1437 at CNRS. One of us (W. S.) is supported by a DAAD Ph.D. fellowship.

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