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Dynamics of anti-Stokes photoluminescence in type-II $Al_xGa_{1-x}As$-$GaInP_2$ heterostructures: The important role of long-lived carriers near the interface

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We have studied the anti-Stokes photoluminescence (ASPL) of a type-II $Al_xGa_{1-x}As$-$GaInP_2$ heterojunction. We have found that the ASPL can appear in both layers adjacent to the heterojunction when the excitation photon energy is higher than the energy of below-band-gap (BBG) luminescence. The intensity of $GaInP_2$-related ASPL shows an almost linear dependence on the excitation intensity. Time-resolved photoluminescence experiments reveal that the ASPL can be sustained as long as the BBG luminescence remains. Our results suggest that the energy up conversion for the ASPL is via a two-step two-photon absorption process involving localized, long-lived carriers near the type-II interface. [S0163-1829(97)52832-3]

Anti-Stokes photoluminescence (ASPL) or photoluminescence (PL) up conversion, a phenomenon in which the photon energy of PL output is higher than the excitation energy, in heterojunctions (HJ's) and quantum wells (QW's) has attracted considerable attention recently.[1–6] The energy up conversion in bulk semiconductors is usually achieved by (i) a momentum-conserving Auger process, (ii) an interaction with the thermally populated phonon modes as in the anti-Stokes Raman shift, or (iii) a nonlinear mechanism such as two-photon absorption (TPA) via real or virtual states.[7] The Auger recombination process, in which an electron recombines with a hole by transferring the excess energy immediately to another electron or hole, is responsible for the nonradiative recombination in bulk semiconductors.[8] The TPA process via virtual states can occur at high excitation densities ($\geqslant 10^3$ W cm^{-2}).[9] The ASPL phenomena in HJ's or QW's, on the other hand, can be observed with an extremely small excitation density of $P_{ex} \simeq 0.1$ W cm^{-2} at low temperature ($T \leqslant 10$ K).[1–6]

The ASPL in HJ's and QW's has a wealth of proposed mechanisms, some of which are in direct conflict with each other. Seidel *et al.*[2] observed that the integrated ASPL intensity I_{AS} from the InP side in type-II InP-$AlInAs_2$ HJ's depends on I^2 and α^2, where I is the excitation intensity and α is the interface absorption coefficient. They have proposed the following ''Auger fountain'' process to explain the observed ASPL phenomena: high-energy holes are generated by the Auger recombination process and are then redistributed in a different band or in a different part of the sample in the thermalization process. Electrons recombine with these high-energy holes, and photons with the energy higher than the excitation energy are emitted. They have argued that the dependence of I_{AS} on I^2 and α^2 is experimental evidence supporting their model. Driessen *et al.*[3] have also ascribed the ASPL phenomena in GaAs-(ordered)$GaInP_2$ QW's to the cold Auger process via interface states. To support their claim, they have shown that I_{AS} depends on temperature according to the weak power law as theoretically predicted by Zegrya and Kharchenko.[10]

Hellman *et al.*,[4] on the other hand, have argued that the ASPL in CdTe-(Cd,Mg)Te QW's is due to the two-step TPA process via localized exciton states or via excitons bound to impurities since their results show that I_{AS} is proportional to $I^{2.1}$ and $I^{1.08}$ for lower and higher excitation densities, respectively. They have also suggested that the photons necessary for the second absorption step can be provided by a photon recycling due to the radiative recombination of QW excitons. Su *et al.*[5] and Zeman *et al.*[6] have also proposed a similar two-step TPA process to explain the ASPL phenomena occurring in the GaAs-(ordered)$GaInP_2$ HJ's and established a type-II band lineup as a key element for explaining the observed up conversion. We note that most of the earlier works on HJ's relied mainly on the excitation power-dependent PL data without any direct observation of time-resolved PL (TRPL) emission. Some controversies in the proposed ASPL mechanisms seem to remain partly because of this reason.

In this paper, we report on the ASPL phenomena in a type-II $Al_xGa_{1-x}As$-$GaInP_2$ single HJ. ASPL comes from both layers if the excitation energy is higher than the energy of the interface-related below-band-gap (BBG) PL peak. I_{AS} is found to be nearly proportional to I when the excitation photon energy is larger than the $Al_xGa_{1-x}As$ band-gap energy. TRPL experiments show that the long-lived BBG PL mainly contributes to the ASPL. Thus we suggest that the observed ASPL in the type-II HJ is primarily due to the two-step TPA process mediated by carriers localized near the interface.

We have chosen $Al_xGa_{1-x}As$-$GaInP_2$ HJ's for the study of ASPL phenomena since this HJ system forms either a type-I (straddling) or type-II (staggered) band lineup depend-

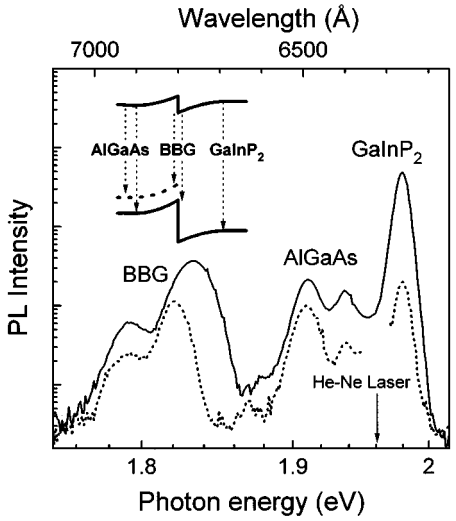

FIG. 1. Photoluminescence spectra of type-II $Al_{0.32}Ga_{0.68}As$-$GaInP_2$ heterojunction using Ar^+ (solid line) and He-Ne lasers (dotted line). The band structure of the heterojunction and the recombination paths for the observed PL peaks are also depicted. The $GaInP_2$-related ASPL is clearly observable under the He-Ne laser excitation.

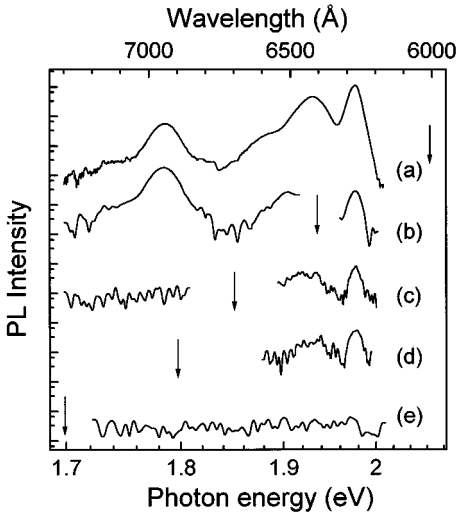

FIG. 2. Photoluminescence spectra of type-II $Al_{0.32}Ga_{0.68}As$-$GaInP_2$ heterojunction for various injection photon energies of a: 2.07 eV; b: 1.94 eV; c: 1.85 eV; d: 1.8 eV; and e: 1.7 eV. Monochromatic light dispersed from a halogen lamp is used as the excitation source. $GaInP_2$- and $Al_{0.32}Ga_{0.68}As$-related ASPL output is clearly observable in c and d spectra.

ing on the Al composition x. The band lineup transition occurs at about $x=0.12$.[11,12] In type-II $Al_xGa_{1-x}As$-$GaInP_2$ HJ's, electrons are confined to the $GaInP_2$ side and holes to the $Al_xGa_{1-x}As$ side, as shown in the inset of Fig. 1. The BBG luminescence due to these spatially separated electrons and holes has a high quantum efficiency and a very long lifetime of about 40–200 ns.[13] $Al_xGa_{1-x}As$-on-$GaInP_2$ HJ's lattice matched to (100) n^+-GaAs substrates were grown at 790 °C by liquid phase epitaxy using a horizontal slider system. Thus our $GaInP_2$ layer is almost fully disordered and the contribution of metastable states induced by the ordering effect on the ASPL (Refs. 3 and 5) should be negligible. All the grown epilayers were n type and the carrier concentrations were of the order of 10^{16} cm^{-3}. The detailed growth conditions were reported elsewhere.[12] An Ar^+ laser and a He-Ne laser were used as excitation sources for cw PL measurements. The monochromatic light dispersed from a halogen lamp was also used to scan the photon energy. All PL measurements were carried out at 10 K. TRPL decay profiles were obtained by using a time-correlated single-photon counting technique with a time resolution of 10 ps.[14] The light source for *pulsed* PL and TRPL was a cavity-dumped dye laser synchronously pumped by a mode-locked Ar^+ laser.

Figure 1 shows two typical PL spectra at 10 K of a type-II $Al_{0.32}Ga_{0.68}As$-$GaInP_2$ single HJ excited by an Ar^+ laser (solid curve) and a He-Ne laser (dotted curve). PL peaks at the energies of 1.98 and 1.94 eV correspond to the near-band-edge transitions of $GaInP_2$ and $Al_{0.32}Ga_{0.68}As$, respectively. The peak at 1.91 eV is due to the band-to-acceptor transition in $Al_{0.32}Ga_{0.68}As$. Two broad peaks at about 1.83 and 1.79 eV are the interface-related BBG PL peaks due to the electronic transitions from the conduction band in $GaInP_2$ to the valence band and the acceptor level in $Al_{0.32}Ga_{0.68}As$, respectively.[11,13] The shift of the 1.83 eV peak to lower energy by about 10 meV under the He-Ne laser excitation is due to the difference of band filling effects under the two cw laser excitations.[11] The PL spectrum excited by the He-Ne laser clearly shows the ASPL coming from the $GaInP_2$ side in addition to the PL spectra from the $Al_{0.32}Ga_{0.68}As$ side and the BBG recombination. The integrated intensity of ASPL I_{AS} has a maximum value of about 30% of the total PL output. We have observed that all the other type-II $Al_xGa_{1-x}As$-$GaInP_2$ HJ's with various x value also show extremely high ASPL efficiencies. On the other hand, a much lower ASPL efficiency is found in the type-I $Al_xGa_{1-x}As$-$GaInP_2$ HJ's where the BBG luminescence is absent (not shown here).

To clarify the physical origin of the highly efficient ASPL in our type-II HJ, we monitored the line shape of ASPL output while varying the excitation photon energy using the dispersed output of a halogen lamp (Fig. 2). Curves c and d clearly show that the ASPL occurs not only in the $GaInP_2$ side but also in the $Al_{0.32}Ga_{0.68}As$ layer when the excitation energy is lower than the PL peak energy of $Al_{0.32}Ga_{0.68}As$ and higher than the energy of BBG PL peaks. However, no ASPL is observed if the excitation energy is lower than the energy of BBG-related PL peaks (curve e). These results imply that the excitation energy corresponding to the spatially indirect electron transition from the potential well in the $GaInP_2$ side to the acceptors in $Al_{0.32}Ga_{0.68}As$ is the threshold energy for the observation of ASPL. We also note from curve c that the ASPL can appear even if the BBG luminescence is negligible, i.e., the up conversion for ASPL can be more efficient than the BBG luminescence. This is quite surprising since electrons (holes) must overcome the barrier of about 130 (170) meV to display the $Al_{0.32}Ga_{0.68}As$- ($GaInP_2$)-related ASPL.[12] Thus the results of Fig. 2 show that the ASPL is closely related to the BBG luminescence but it could also be caused by some other mechanisms.

The possible mechanism for the energy up conversion is first sought from the dependence of I_{AS} on the excitation

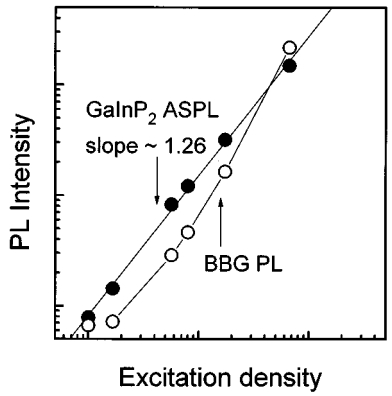

FIG. 3. The dependence of $GaInP_2$ ASPL and BBG PL on the He-Ne laser beam intensity I. The ASPL intensity depends on $I^{1.26}$ but the intensity of BBG PL increases more rapidly as the excitation intensity is increased.

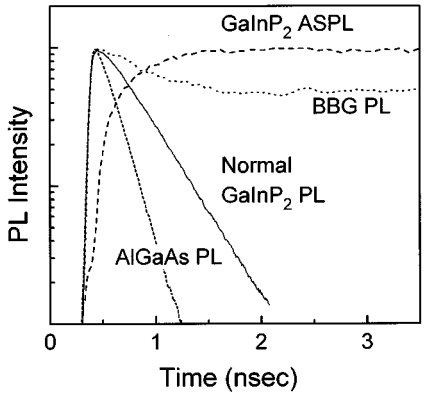

FIG. 4. Time-resolved PL spectra of the type-II $Al_{0.32}Ga_{0.68}As$-$GaInP_2$ heterojunction with $h\nu = 2.11$ eV (solid curve) and 1.96 eV (other curves). The normal $GaInP_2$ PL (solid curve) and $Al_{0.32}Ga_{0.68}As$ PL (short dashed curve) decay very fast but $GaInP_2$ ASPL (dashed curve) and BBG PL (dotted curve) show virtually no decrease within 3 ns.

intensity I of the He-Ne laser. As shown in Fig. 3, the $GaInP_2$-related I_{AS} behaves as I by $I^{1.26}$ over about three decades, whereas the intensity of BBG luminescence grows as I^{β} where β is an increasing function of excitation density. Our results are quite different from those obtained by Seidel *et al.*[2] According to them, the InP-related I_{AS} in InP-AlInAs type-II heterojunction shows an I^2 dependence while the BBG PL intensity depends linearly on I. They have argued that the I^2 dependence of InP-related I_{AS} is one of the main evidences that the energy up conversion is carried out by the cold Auger process. In our case, on the contrary, the fact that I_{AS} does not show an I^2 dependence indicates that the cold Auger process would not be the main energy up-conversion mechanism in the $Al_xGa_{1-x}As$-$GaInP_2$ heterointerface. Furthermore, if the cold Auger process were the main energy up-conversion process, the ASPL from one side of the sample would prevail since one of the electron-electron-hole or the electron-hole-hole collision processes would be dominant.[8] Note that the energy up conversion by the thermal excitation of the photogenerated carriers or by the TPA via virtual states must also be ruled out since our experiments were performed at about $T = 10$ K under a very small excitation density of about $0.01 \sim 0.1$ W/cm^2. A more plausible energy up-conversion mechanism for our $GaInP_2$ ASPL must be the two-step TPA process via localized states near the interface.[4,5] As Hellmann *et al.* have pointed out,[4] the photogenerated electrons and holes can survive long enough forming bound excitons and can be excited once again by other photons. In the second excitation process, the photons can be provided by the excitation beam or by the luminescence (photon recycling). In our case, the BBG luminescence is one of the main undergoing recombination processes under the He-Ne excitation (Fig. 1). The lifetime of the photogenerated carriers is very long[13] because the electron and the hole wave functions are spatially separated. Thus, these long-lived electrons and holes localized near the interface would have enough chances to be excited by the other excitation photons or by the luminescence photons.

The fact that $I_{AS} \propto I^{1.26}$ means that the up-conversion efficiency due to the excitation beam is essentially constant in our range of excitation density. If the energy up conversion stems from the two-step TPA process, the I_{AS} is proportional (i) to the population of the intermediate states (N_{int}) and (ii) to the number of photons inducing the second absorption step (N_{ph}). For the electrons to be excited to the high-energy states by the second photon absorption without phonon assistance, the wave functions of the electrons must be composed of a large range of k values in the Brillouin zone. Thus, only limited and well-defined portions of the carriers near the interface can contribute to the second absorption process. Since the carriers generated in the $Al_xGa_{1-x}As$ side by the excitation of the He-Ne laser (1.96 eV) flow into the interface, the population of this limited number of bound states responsible for the second absorption would become saturated at relatively lower excitation intensities. The intensity of the BBG PL, which is believed to be one of the major excitation sources for the energy up conversion, shows an excitation density dependence somewhat higher than I (Fig. 3). This might be due to the enhancement of the wave-function overlap between electrons and holes near the interface caused by the band bending and the band filling effects at high excitation density.[13,15] This increased wave-function overlap can then lead to a higher recombination rate and PL efficiency. The fact that ASPL maintains $I^{1.26}$ dependence whereas the BBG PL steeply increases then reflects that the N_{int} becomes saturated as N_{ph} is increased.

The energy up-conversion procedure is more directly monitored by TRPL experiments shown in Fig. 4. The normal $GaInP_2$ PL induced by the photons with the energy of 2.11 eV decays very fast. But the PL peaks show quite different decay behaviors when the excitation photon energy is 1.96 eV. The normal $Al_{0.32}Ga_{0.68}As$ PL peak at 1.94 eV also decays very fast within 1 ns, similar to the normal $GaInP_2$ PL under the excitation energy of 2.11 eV. However, the $GaInP_2$ ASPL and the BBG PL show virtually no decrease within 3 ns. We have verified that the ASPL is sustained as long as the BBG PL remains and these two PL peaks survive simultaneously for more than about 100 ns (which is more than 2 orders of magnitude longer than that of the normal PL) with almost *the same decay time*. Furthermore, the rise time of the $GaInP_2$ ASPL is much longer than that of the BBG PL and similar to the fast decay part of the BBG PL with about 1 ns. This suggests that during the fast decay time (~ 1 ns) of the BBG PL caused by the recombination of the electrons and

the holes near the interface, the photons from the BBG PL excite holes from the $Al_{0.32}Ga_{0.68}As$ side into the $GaInP_2$ side. It should be noted that this delayed rise time of ~ 1 ns for the ASPL is consistent with our proposed mechanism of the two-step absorption process via intermediate states, since carriers should first relax down to the intermediate states responsible for the two-step absorption and then would be excited to the higher energy states. To our mind, however, it is unlikely that the time delay is expected in its rise in the band-to-band Auger process proposed by the earlier works, since the holes should be excited to the higher energy states *instantaneously* with the emission of the BBG PL. The carriers necessary for the BBG PL can be supplied once again by the absorption of the ASPL via a photon recycling process, and hence a quasithermal equilibrium is established between the holes on the $Al_xGa_{1-x}As$ side and the holes on the $GaInP_2$ side. The BBG PL and the ASPL can thus survive simultaneously for a long time even when the excitation source is extinct and the normal PL output has decayed already, which is manifested by the identical temporal decay of the BBG PL and the ASPL. All these facts strongly indicate that most photons inducing $GaInP_2$ ASPL are supplied by the long-lived BBG luminescence and thus such a highly efficient $GaInP_2$ ASPL is possible.

The fact that the energy up conversion is mainly due to the photon recycling can explain other experimental observations. The time-integrated output of $GaInP_2$-related ASPL reaches up to about 18% of total PL output when the same sample is excited by a pulse of 1.96 eV photons using a cavity-dumped dye laser with a 2 ps pulse width at a 1.5 MHz dumping rate. In this case, the excitation photons cannot be used in the energy up-conversion process since all the carriers generated by the previous photon pulse recombine in a time interval much shorter than the repetition time of 660 ns. In addition, the 2 ps of the pulsewidth is not enough for the photogenerated carriers to relax to the bound states (Fig. 4). Thus the photons inducing the second absorption must be supplied from the BBG luminescence. The fact that the ASPL appears in both the $GaInP_2$ and $Al_xGa_{1-x}As$ side even when the BBG PL is not observable (Figs. 2 c, d) may also indicate that the energy up conversion is mainly accomplished by absorbing the photons coming from the BBG PL. In these cases, the carrier concentration confined near the interface should be very low due to a small absorption strength at the type-II single heterointerface for the energies between BBG and $Al_xGa_{1-x}As$ band gaps.[2,15] Thus the intensity of the BBG PL should be small under these excitation conditions even if the photons of the BBG PL are not used in the energy up-conversion process. If most of the photons coming from the BBG PL are used in the energy up-conversion process, it will finally make the BBG PL intensity lower than the detection limit of our instruments and the intensity of the ASPL higher than that of the BBG PL.

In summary, we have studied the dependence of ASPL of the type-II $Al_xGa_{1-x}As$-$GaInP_2$ heterojunction on the photon energy and the excitation density. The results suggest that the energy up conversion for the ASPL is due to the two-step TPA process via localized electrons and holes. TRPL experiments show that the only energy source for the long-lived ASPL is the interface-related BBG luminescence.

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