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Photoluminescence up-conversion in GaAs/$Al_xGa_{1-x}As$ heterostructures

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We propose GaAs/$Al_xGa_{1-x}As$ heterostructures as a model system to study the phenomenon of photoluminescence (PL) up-conversion and demonstrate low-temperature up-converted PL (UPL) in these heterostructures. We find that a mechanism to prevent up-converted carriers in the $Al_xGa_{1-x}As$ layer from thermalizing back to the GaAs layer is essential for efficient UPL. We also find that neither a type-II band alignment nor existence of long-lived intermediate states is an essential requirement of UPL. The results of time-resolved UPL measurements are interpreted within the current models. [S0163-1829(98)50932-0]

Photoluminescence (PL) up-conversion in semiconductor heterostructures (HS's), where luminescence occurs at energies higher than that of the excitation photons, has been a subject of intense interest recently.[1–10] The GaAs/ordered-(Al)$Ga_xIn_{1-x}P$ heterojunctions (HJ's),[4,6–9] in particular, have attracted much attention due in part to very large energy gains (up to 700 meV),[6] leading to emission in the technologically important red-green region of the spectrum. Here, luminescence from spontaneously ordered[11] (Al)$Ga_xIn_{1-x}P$ ($\sim$1.9–2.2 eV) was observed when these HJ's were excited with photons with an energy just higher than the band gap of GaAs (1.519 eV). Up-converted PL (UPL) requires that (i) there exists a mechanism that ''up-converts'' electrons and/or holes from the low-band-gap material to the high-band-gap material and (ii) such up-converted carriers do not relax back to the low-band-gap material before they radiatively recombine. As for the first requirement, the so-called cold-Auger process[1,2,4,6,12] and the two-step, two-photon absorption (TS-TPA) process with[3,9] or without[7,8] photon recycling, are most frequently suggested as the up-conversion mechanism. To meet the second requirement, there should be a localization mechanism for carriers in the higher-band-gap material. This can be provided by band bending in type-II heterojunctions.[2,9] In type-I heterojunctions, the higher-band-gap material itself should have a localization mechanism. For ordered (Al)$Ga_xIn_{1-x}P$ alloys, local fluctuation in the band-gap energy due to short-range clustering,[6] or variations in the degree of ordering[13,14] and/or alloy composition has been suggested as such a mechanism. This interpretation was supported by the lack of an UPL signal in GaAs/random-alloy $Ga_xIn_{1-x}P$ HJ's.[4]

However, problems in the GaAs/(Al)$Ga_xIn_{1-x}P$ materials system make it unsuitable as the prototypical system to study the physics of UPL: the quality of the GaAs/$Ga_xIn_{1-x}P$ interface is strongly dependent on the details of the growth conditions.[15] Since the up-conversion process is thought to be interface-related in both major models, possible variations in the interface quality make it difficult to compare different samples. Also, the spontaneous ordering phenomenon in (Al)$Ga_xIn_{1-x}P$ significantly modifies the band structure, and thus influences important parameters such as the band offsets between GaAs and (Al)$Ga_xIn_{1-x}P$, making it difficult to compare different samples. For example, it has been suggested that the band offset between GaAs and $Ga_xIn_{1-x}P$ can be either type-I or type-II depending on the degree of ordering.[16,17] Recently, Zeman *et al.* claimed that all GaAs/$Ga_xIn_{1-x}P$ HJ samples that exhibit UPL have a type-II band offset.[8] If this is the case, the lack of UPL in GaAs/random-alloy $Ga_xIn_{1-x}P$ could be due to a type-I alignment or due to the lack of a localization mechanism as Driessen *et al.* asserted.[4,6] It is evident that eliminating the uncertainty regarding the band alignments will be essential in studying the physics of UPL.

In this paper, we use GaAs/$Al_xGa_{1-x}As$ HS's as a model system to study the UPL phenomenon and report on the observation of UPL in various GaAs/$Al_xGa_{1-x}As$ HS's. Observations of UPL in GaAs/$Al_xGa_{1-x}As$ HS's have been reported in the literature.[1,5,10] However, in these cases, the UPL signal, usually at $\leqslant$50 meV above the excitation energy, originates from higher energy levels in the GaAs quantum wells (QW's), and not from the $Al_xGa_{1-x}As$ barrier layers. Therefore, it is questionable whether the UPL mechanism in these structures could be the same as that in the GaAs/(Al)$Ga_xIn_{1-x}P$ HS's. In this study, we seek to observe UPL from $Al_xGa_{1-x}As$ layers so that one can make a comparison with the case of GaAs/(Al)$Ga_xIn_{1-x}P$ HS's. A series of samples with different heterojunctions were designed, as shown schematically in Fig. 1. The first sample (A) that serves as a reference, consists of a 1000-Å $Al_{0.18}Ga_{0.82}As$ layer between a GaAs buffer layer and a GaAs cap. In the second sample (B), the $Al_{0.18}Ga_{0.82}As$ layer is replaced with a disordered superlattice (DSL)[18,19] consisting of a random sequence of 10-Å-thick $Al_{0.15}Ga_{0.85}As$ and $Al_{0.20}Ga_{0.80}As$ layers. The randomness of the superlattice period creates localized states for electrons and holes,[18,19] mimicking the carrier localization in ordered (Al)$Ga_xIn_{1-x}P$ alloys. In the third sample (C), 300-Å $Al_{0.3}Ga_{0.7}As$ layers are inserted between a 1000-Å $Al_{0.19}Ga_{0.81}As$ layer and the

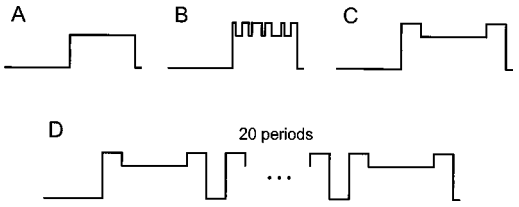

FIG. 1. Schematic diagrams of GaAs/$Al_xGa_{1-x}As$ HS's used. Only the conduction band edge is shown for simplicity.

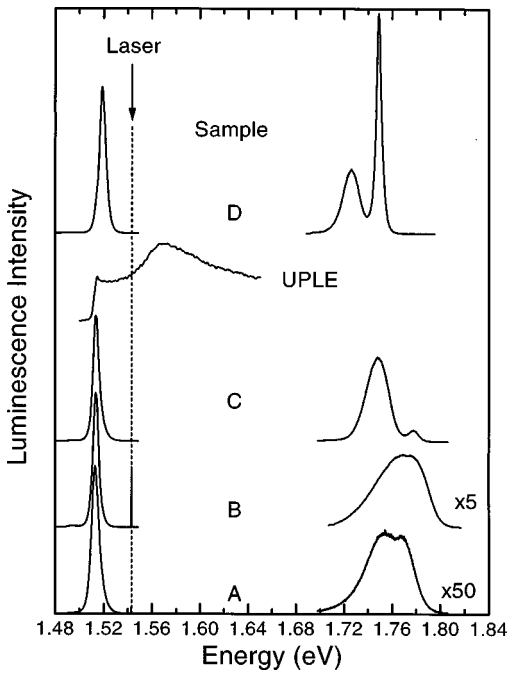

FIG. 2. Luminescence spectra of the samples for the indicated excitation laser energy. UPL signals are seen near 1.75 eV for all samples. UPLE spectrum for Sample C is also shown.

GaAs layers, forming a $Al_{0.19}Ga_{0.81}As/Al_{0.3}Ga_{0.7}As$ wide QW. The $Al_{0.3}Ga_{0.7}As$ layers serve as barriers that prevent relaxation of carriers from the $Al_{0.19}Ga_{0.81}As$ layer to the GaAs layers. The last sample (Sample D) consists of 20 periods of an $Al_{0.17}Ga_{0.83}As/Al_{0.3}Ga_{0.7}As$ structure similar to that of Sample C, separated by 300-Å GaAs layers. Here, photocarriers are created and confined in the 300-Å GaAs QW layers until they recombine or up-convert. The confinement of carriers in GaAs and the increased total volume of the UPL-emitting $Al_xGa_{1-x}As$ layer are expected to result in an increased UPL intensity. The samples were grown by low-pressure (75 torr) metal-organic chemical vapor deposition (MOCVD) at 750 °C. All layers were nominally undoped and were grown on semi-insulating GaAs (001) substrates. The structures were grown on a 0.5–1.0 μm GaAs buffer layer and all samples were capped with 100 Å of GaAs.

UPL measurements were performed at 10 K with a cw titanium:sapphire laser at 8034 Å (1.543 eV) as the excitation. An RG780 long-pass filter was placed in the laser beam path in order to prevent the short-wavelength tail of the titanium:sapphire luminescence from exciting $Al_xGa_{1-x}As$ PL directly. The UPL signal was dispersed by a 0.6-m triple spectrometer and detected with a liquid-nitrogen-cooled charge-coupled device (CCD) array. Figure 2 shows luminescence spectra of the four samples. For each sample, a UPL signal is observed at $\gtrsim$200 meV above the excitation energy, indicated by an arrow. Much stronger GaAs PL (scaled down by a factor of 30 000) is seen at the GaAs exciton energy at 1.515 eV for Samples A, B, and C, and at a slightly higher energy for Sample D due to the confinement effect of the 300-Å GaAs QW's. As expected, Sample A shows the weakest UPL signal. Although there is no confinement of up-converted carriers, the relatively large thickness (1000 Å) of the $Al_xGa_{1-x}As$ layer allows some of the up-converted carriers to radiatively recombine before they can relax back to GaAs by diffusion. This is probably why UPL has not been observed in $GaAs/Al_xGa_{1-x}As$ HS's, where the $Al_xGa_{1-x}As$ layers are typically less than 500 Å thick. Sample B, where the up-converted carriers in the DSL layer are localized, shows UPL ~10 times stronger than that of Sample A. This demonstrates the importance of a localization mechanism in the UPL process. Sample C shows even stronger UPL (~5 times stronger than Sample B). In this case, up-converted carriers are confined in the $Al_{0.19}Ga_{0.81}As$ layer by the $Al_{0.3}Ga_{0.7}As$ barriers, which should be more effective in preventing carriers from thermalizing back to the GaAs layers than the DSL. Sample D shows the strongest UPL (about twice stronger than Sample C), as expected. Both PL spectra for Samples C and D show an excitonic peak at higher energies and a shallow-impurity related peak at lower energies, typical of good quality undoped $Al_xGa_{1-x}As$. The excitonic peak is relatively stronger in Sample D, probably due to the improved quality[20] of the topmost $Al_xGa_{1-x}As$ layers that are most responsible to the UPL. The UPL intensities of Samples C and D are comparable to that of a typical GaAs/ordered-$Ga_xIn_{1-x}P$ sample. A UPL excitation (UPLE) spectrum of Sample C is also shown in Fig. 2. Here, the excitation photon energy of the titanium:sapphire laser, passed through an RG715 long-pass filter, is scanned while the UPL signal at 1.749 eV was monitored by a cooled photomultiplier tube after being dispersed by a 0.85-m double monochromator. The UPLE spectrum shows a clear onset at the GaAs exciton energy, giving direct evidence that the carriers that are recombining to give UPL are created by photoabsorption in GaAs, and is consistent with what has been observed in UPLE spectra of GaAs/ordered-$(Al)Ga_xIn_{1-x}P$ HJ's.[4,6,7]

The carrier dynamics of the UPL process is studied for Sample D with time-resolved detection at each stage of the UPL process: GaAs PL, $Al_{0.19}Ga_{0.81}As$ PL, and UPL, all at 5 K. An ultrafast laser and time-resolved single photon counting yield a resolution of 55 ps. When an ultrafast laser is used in the study of UPL, special attention needs to be paid to avoid contributions to the UPL signal from nonlinear optical processes such as second-harmonic generation (SHG) or two-photon absorption (TPA) that can create carriers directly in $Al_xGa_{1-x}As$. Since the contributions from these processes, unlike the UPL process, should not have a sharp onset at the band-gap of GaAs, these contributions can be checked by varying the excitation energy across the GaAs band gap. SHG from $GaAs/Al_xGa_{1-x}As$ grown on (001) GaAs substrates can be suppressed by choosing a normal incidence angle for the laser, but it is more difficult for GaAs/ordered $(Al)Ga_xIn_{1-x}P$ due to the trigonal symmetry of ordered $(Al)Ga_xIn_{1-x}P$.[21] In this study, we used normal incidence geometry and detected no SHG signal from the sample. On the other hand, since TPA is nearly isotropic in these conditions, it is impossible to eliminate the TPA signal completely. However, since TPA is a quadratic function of the *instantaneous* laser power, while the UPL mechanism depends on the carrier density which in turn depends on the *average* laser power, the relative ratio of the TPA contribution to the total UPL signal can be reduced by using a longer pulse width for a given average power. In our study, the GaAs PL and the UPL were both excited with 3

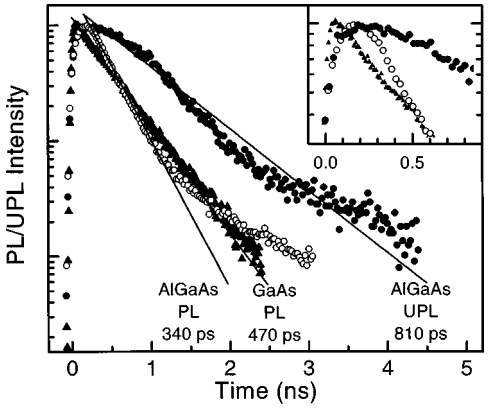

FIG. 3. Time-resolved 5-K luminescence from Sample D: GaAs PL detected at 1.512 eV (triangles), $Al_xGa_{1-x}As$ PL detected at 1.747 eV (open circles), and UPL of the HS also detected at 1.747 eV (solid circles). Solid lines are single exponential fits. Expanded region around $t=0$ is shown in the inset.

$\times 10^{-4}$ J cm^{-2} of 1.54 eV pulses temporally broadened to a few ps. This broadening of the pulse width reduces the peak power of the laser while maintaining the average power. At broader pulse widths, the luminescence from $Al_{0.19}Ga_{0.81}As$ was observed to be negligibly weak when the laser energy was lowered below the GaAs band gap, which indicates that the TPA contribution to the UPL signal is minimal. The $Al_{0.19}Ga_{0.81}As$ PL was excited with 100-fs, 2.03-eV pulses, with an excitation density adjusted approximately $\times 10^4$ smaller to give a similar magnitude of luminescence from the $Al_{0.19}Ga_{0.81}As$ layer.

Decay traces are shown in Fig. 3. The GaAs PL shows a resolution-limited rise and a single exponential decay, while the $Al_{0.19}Ga_{0.81}As$ PL has a delayed rise and a two-component decay. Slow PL rise times are due to carrier cooling,[22,23] and the long decay component we attribute to extrinsic PL, which is a significant contribution at this low density. The UPL signal has a rise time similar to that of the $Al_xGa_{1-x}As$ PL, a convex, nonexponential decay during the first 2 ns, and a long decay that mimics the long tail of the $Al_xGa_{1-x}As$ PL. The longer overall decay time of the UPL signal is additional evidence that the contributions from SHG or TPA, which should have a decay trace identical to that of the $Al_xGa_{1-x}As$ PL, is minimal. This temporal behavior of the UPL signal is consistent with the current models of the UPL process. As carriers are created and relax to the band edges of GaAs the up-conversion process transfers carriers from GaAs to $Al_xGa_{1-x}As$. Once high-energy carriers are introduced into $Al_xGa_{1-x}As$, the decay dynamics should be identical to that of the $Al_xGa_{1-x}As$ PL. However, since the up-conversion process keeps feeding carriers into $Al_xGa_{1-x}As$ as long as there are carriers in the GaAs layer, the initial decay of the UPL should be significantly slower than that of the $Al_xGa_{1-x}As$ PL. Then, after the carriers in the GaAs layer are sufficiently depleted, introduction of new carriers into the $Al_xGa_{1-x}As$ layer becomes negligible, and the decay characteristics of the UPL signal should mimic the tail of the $Al_xGa_{1-x}As$ PL. All these characteristics are reflected in the shape of the decay trace of the UPL signal. Recently, it was observed that the decay time of the UPL from type-II $Al_xGa_{1-x}As/Ga_xIn_{1-x}P$ heterojunctions was similar to that of the long-lived below-band-gap (BBG) type-II luminescence, which serves as a reservoir for the carriers.[9] This is consistent with our result: the UPL persists as long as carriers are available in the reservoir for up-conversion even long after the laser pulse. However, both this and our result are incompatible with the ''TS-TPA without photon recycling'' model,[7,8] in which a second photon from the laser is required to up-convert holes. In that model, the UPL should have identical decay characteristics as that of the higher-energy material because the laser pulse is essentially a δ function in the time scale of the observed PL/UPL decay.

Our results demonstrate that: (i) one can observe up-conversion of carriers from GaAs to $Al_xGa_{1-x}As$ in type-I $GaAs/Al_xGa_{1-x}As$ HS's, and therefore, these HS's can be used as a model system; and (ii) confinement of carriers to the $Al_xGa_{1-x}As$ layer is essential for efficient UPL. It should be pointed out that: (i) most carriers in the GaAs layers are not localized except for the weak quantum-well confinement in Sample D; and (ii) the intermediate states for the UPL process, the band-edge electron and hole states in GaAs, are not long-lived. Therefore, we conclude that a type-II band offset[8] or existence of long-lived, localized intermediate states[3,9] are not essential requirements of the UPL phenomenon, as has been suggested.

It is appropriate to compare the two most plausible models of the up-conversion process. In the ''cold-Auger'' or ''Auger-fountain'' model,[1,2,4,6] the photons from the laser create electrons and holes in the GaAs layer. These carriers relax to the band edges of GaAs. Then, an electron recombines with a hole, transferring the recombination energy to another electron or a hole (Auger process). Electrons and holes thus up-converted, relax to the band edges of $Al_xGa_{1-x}As$, get trapped in the $Al_xGa_{1-x}As$ layer owing to the localization mechanisms, and then recombine to give UPL. The Auger process, which is very inefficient in the bulk at low temperatures due to momentum (**k**) conservation, is efficient in HS's due to breaking of translational symmetry at the interface. Also, since **k**-conservation is lifted only in the direction perpendicular to the heterointerface, the high-energy up-converted carriers are ejected in that direction, facilitating easy transfer of carriers from GaAs to $Al_xGa_{1-x}As$. In the ''TS-TPA with photon recycling'' model,[3,9] an electron and a hole that are photoexcited and have relaxed to the band edges, recombine to give a photon, which in turn excites another electron or a hole through intraband absorption, creating a high-energy up-converted electron or hole. Again, this is an inefficient process in the bulk at low temperatures but is allowed near a heterointerface owing to lifting of **k**-conservation. These two mechanisms are different in that the second involves emission and reabsorption of a photon and the first does not. However, the two are similar in that both require two electrons (holes) and a hole (electron) in GaAs to create one high-energy electron (hole). Therefore, both should have a similar dependance on the excitation power. Also, they should have similar dynamics for a given HS, because the two processes are almost identical, except for emission and reabsorption of photons in the second process. In reality, both of these two mechanisms should coexist and contribute to UPL in any HS, and it would be difficult to experimentally determine which of the

two is the dominant mechanism for a given HS. So far, the strongest indication has been provided by a collinear two-beam excitation experiment on a GaAs/$Ga_xIn_{1-x}P$ HS,[6] where one laser was used to excite UPL while a second laser was scanned across the GaAs band-gap energy. In the ''TS-TPA with photon recycling'' model, since the intermediate photon can be provided by a photon from the second laser, one should observe an increase in UPL as long as the energy of the second laser is higher than the conduction- and valence-band offsets even if it is lower than the GaAs band gap. However, increase in the UPL signal was observed only when the second laser energy was higher than the GaAs band gap, indicating that the intraband absorption of the TS-TPA model is an inefficient process for this HS. However, it is yet unclear if this argument can be generalized for other HS's. More work in both experiment and theory is needed to determine if one or the other mechanism is the dominant factor for other HS's.

Finally, we comment on the relation between UPL and the band alignment. It has been argued that UPL requires either a type-II band alignment[8] or a small band offset.[7] However, as out study shows, UPL does not require either of these. It is worthwhile to note that in a type-II HJ, only one type of carrier needs to be up-converted to give UPL, and therefore the UPL signal should be stronger than in a similar type-I HJ. Our preliminary measurements on type-II $Al_xGa_{1-x}As/Ga_yIn_{1-y}P$ samples indicate that the UPL from these samples is at least one order of magnitude stronger than that in GaAs/$Al_xGa_{1-x}As$ or GaAs/$Ga_xIn_{1-x}P$. Therefore, type-II HJ's seem more desirable for higher efficiency UPL devices. However, since the theoretical maximum UPL energy is limited to twice the type-II transition energy, while that for a type-I structure is three times the band-gap energy of the lower band-gap material, type-I structures would be more desirable for large energy gains.

In summary, by measuring UPL from GaAs/$Al_xGa_{1-x}As$ HS's, we demonstrate that these HS's can be used as a model system to study the UPL phenomenon. We find that preventing up-converted carriers in the $Al_xGa_{1-x}As$ layer from thermalizing back to the GaAs layer is essential for efficient UPL. We also find that neither a type-II band alignment nor existence of long-lived intermediate states is an essential requirement of UPL. The results of time-resolved UPL measurements are incompatible with the model of ''TS-TPA *without* photon recycling'' but are consistent with the ''cold-Auger'' model or the ''TS-TPA *with* photon recycling'' model.

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