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Band alignment and photoluminescence up-conversion at the GaAs/(ordered)$GaInP_2$ heterojunction

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The up-conversion of photoluminescence in a series of GaAs/(ordered)$GaInP_2$ heterojunctions has been investigated using high magnetic field and high pressure. Samples which exhibit this effect have been demonstrated to have a type-II band alignment and also localization centers in $GaInP_2$ Some samples revealing a type-I band alignment do not show this effect at atmospheric pressure. However, such a sample exhibits up-conversion under a hydrostatic pressure of 1.2 GPa. Our results establish a type-II band alignment as one of the key elements for explaining the observed up-conversion. [S0163-1829(97)50224-4]

It is now well established that the alloy $Ga_xIn_{1-x}P$ where $x \sim 0.50$ (to be abbreviated as $GaInP_2$) forms an ordered natural superlattice with the CuPt structure when grown by metal-organic chemical vapor deposition (MOCVD) on [001] oriented GaAs substrates,[1] whereas a random alloy results from growth by liquid-phase epitaxy. The band gap of ordered $GaInP_2$can be reduced from that of the random alloy by as much as 0.1 eV. Using hydrostatic pressure Chen *et al.*[2] have shown that the band alignment between random $GaInP_2$ alloy and the GaAs substrate is of type I with a conduction-band offset of ~60 meV which is much smaller than the corresponding valence-band offset (about 370 meV). The offset between partially ordered $GaInP_2$and GaAs is less well known. It is usually assumed to be type I also. Recently, Froyen *et al.*[3] have calculated it theoretically for both disordered and completely ordered $GaInP_2$. They predict a type-II band alignment between completely ordered $Ga_xIn_{1-x}P$ and GaAs. However, because real samples are only partially ordered, it is difficult to predict their band alignment precisely.

Since the report by Driessen[4] of a rather efficient up-conversion of near-infrared photons (energy near the band gap of GaAs) into visible photons (energy near the band gap of $GaInP_2$) with fairly low power cw lasers, there is a debate about the mechanism responsible for this effect. Understanding this mechanism is important for possible applications of this phenomenon in devices such as uv lasers or infrared detectors. Driessen[4] has proposed Auger processes at a type-I GaAs/$GaInP_2$ interface as the relevant mechanism. Su *et al.*[5] have instead suggested a two-step two-photon absorption (TS-TPA) process since they observed up-conversion even when only holes localized on acceptors are excited. In this model, a type-II band alignment would facilitate the photoluminescence up-conversion (PLU). Thus, to distinguish between these two mechanisms it is important to determine the band alignment of both samples which exhibit PLU and those that do not. In this investigation, we use high-magnetic-field and high-pressure techniques to demonstrate a strong correlation between PLU and a type-II band alignment. In particular, a sample exhibiting no PLU at atmospheric pressure has been made to do so by the application of pressure which tends to produce a type-II band alignment in this system. Our results suggest that the TS-TPA mechanism involving a type-II band alignment is responsible for the efficient PLU at the GaAs/$GaInP_2$ interface. We note that the processes reported recently in Ref. 6 and involving localized excitons in type-I quantum wells are different from the TS-TPA mechanism.

We have studied a series of $GaInP_2$ epilayers of thickness ~1 μm grown by MOCVD on a p-type GaAs buffer layer deposited on a [001] oriented semi-insulating GaAs substrate. The growth temperature varies between 650 and 750 °C while the V-III ratio varies between 100 and 400. The lattice mismatch between the epilayer and the GaAs substrate is typically about 10^{-3} or less. When excited by the 2.41-eV (514.5 nm) line of an Ar^+ laser at liquid-He temperature the ''normal'' photoluminescence (NPL) spectra of these samples exhibit excitonic peaks varying between 1.88 and 1.93 eV, indicating different degrees of partial ordering in these samples as confirmed independently by electron diffraction patterns. ''Up-converted'' photoluminescence (PL) excited with either the 1.60-eV output of a Ti:sapphire laser or the 1.834-eV line of a Kr^+ laser was observed in three of the samples grown under different temperatures. There seems to be no correlation between the degree of ordering and the presence of PLU. The power density on the samples was typically about 1 W/cm^2. The emission spectra were analyzed by a triple DILOR XY spectrograph equipped with an optical multichannel detector. Magnetic field up to 23 T

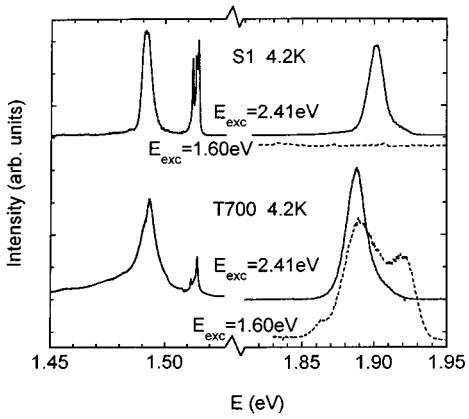

FIG. 1. Emission spectra of T700 and S1 in both the GaAs region (around 1.50-eV region) and the $GaInP_2$ region at 0 T and 1 bar. The broken curves show the up-converted photoluminescence.

was applied by a modified resistive Bitter magnet while high pressure was generated with a diamond anvil cell using a standard methanol/ethanol mixture as the pressure medium.

Here we shall concentrate on the results obtained from two samples labeled T700 and S1. They have been grown at the same temperature but with a different V-III ratio. In Fig. 1 we compare their NPL spectra excited by the Ar^+ laser and also their upconverted PL excited by a 1.60-eV photon energy laser. While T700 exhibits strong PLU, S1 shows no sign of PLU at even high excitation intensities. We note that the up-converted spectrum is broader than the NPL spectrum and can be deconvoluted into a superposition of at least two Gaussian peaks. The relative intensities of these peaks depend on the excitation wavelength and power density. For completeness we show in Fig. 1 also the PL spectra of GaAs measured under the same conditions as the $GaInP_2$ spectra. Figure 2 shows the evolution of the different spectra with high magnetic field (B) for a constant excitation power density. We notice that at moderate fields the low-energy peak (at 1.49 eV at 0 T) splits into two components with different linewidths: a narrow peak at 1.492 eV and a broader one at 1.489 eV. The latter grows in intensity at the expense of the former until at 20 T the broader peak becomes dominant.

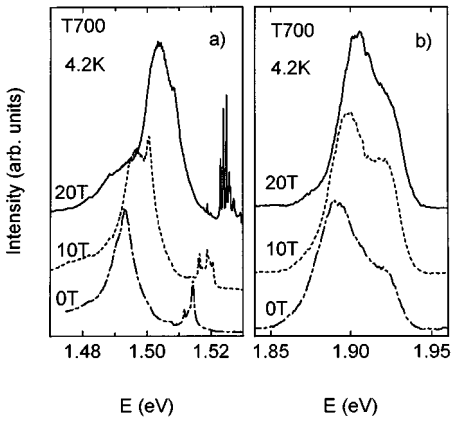

FIG. 2. The magnetic-field-dependent emission spectra of T700 in (a) the GaAs band-gap region and (b) the $GaInP_2$ band-gap region when excited by photons of 1.60 eV.

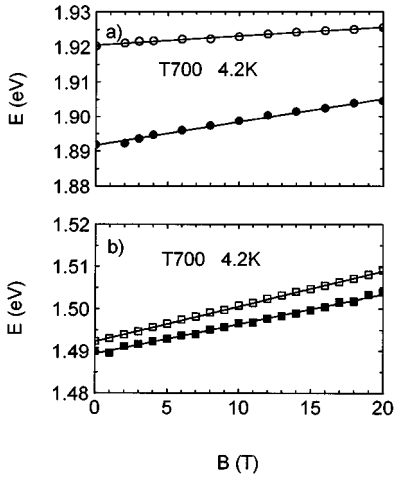

FIG. 3. Plot of the deconvoluted peak energies (see text) vs B in T700 for (a) the up-converted spectra of $GaInP_2$ and (b) the 1.49-eV structure in GaAs. The solid lines are least-square fits of the data points with a straight line.

The up-converted $GaInP_2$ peak behaves differently. Its two components appear to merge together as B is increased.

By deconvoluting the emission peaks in Fig. 2 we obtain their magnetic-field dependence as shown in Fig. 3. Unlike the *quadratic* field dependence of the excitonic peak in the NPL spectra of $GaInP_2$ reported previously,[7] the structures in the upconverted spectra exhibit a *linear* field dependence [Fig. 3(a)]. A linear variation with a field of such an optical recombination is usually assigned to either a transition involving a free electron and a free hole, or a free carrier and a localized carrier. In the former case, the linear field dependence is given by $eB/(2\mu)$ where μ is the reduced mass of the electron and hole. In the latter, the linear field dependence is determined by the carrier mass m^* via $eB/(2m^*)$ assuming that the localized carrier has a negligible Zeeman splitting. From the slope of the fitted linear relation to the data points, we find that[8] the higher-energy peak involves a *localized* electron and a free hole (effective mass m_h^* equal to $0.24m_0$) while the lower-energy peak is attributed to a recombination of a *localized* hole with a free electron (effective mass m_c^* equal to $0.084m_0$). The possibility that the observed transitions involve two free carriers is eliminated by the fact that the known reduced mass in $GaInP_2$ disagrees with their field dependence. Furthermore, the free carrier masses are determined based on the second interpretation, and are in good agreement with the values of ~ 0.25 and $\sim 0.09m_0$ reported previously by Jones *et al.*[7] We should point out that the other samples which show PLU all exhibit similar *linear* magnetic-field dependence and the same masses for the electrons and holes in $GaInP_2$ although their up-converted emission peak energies may differ. The linear magnetic-field dependence of the PLU peaks is strong evidence that at least one *localized* carrier is involved in the up-converted emission, consistent with the suggestion of Driessen.[4]

A similar analysis of the low-energy portion of the GaAs emission spectra around 1.49 eV in sample T700 leads to the linear magnetic-field dependence shown in Fig. 3(b). This suggests that a free and localized carrier is also involved in

each of these transitions. From the slope of the least-square linear fits to the data, their effective masses are determined to be $0.07m_0$ and $0.084m_0$, respectively, for the high-energy and low-energy peaks. Similar results and almost identical masses are obtained from the other samples which exhibit PLU. The higher-energy component can be identified as due to the radiative recombination between a free electron in the conduction band of GaAs (effective mass equal to $0.067m_0$) and a hole localized on an acceptor. The interesting result is that the mass of the carrier associated with the *lower-energy* peak suggests that it involves a free electron in the *conduction band of* $GaInP_2$ recombining with a localized hole in GaAs. The relative energies of these transitions suggest a *type-II band alignment*. This proposal is consistent with the change in intensities of those two peaks with magnetic field as a result of thermalization. In principle, a band offset of about 3 meV can be deduced from the zero-field splitting of these two peaks. In practice it is necessary to consider effects such as those associated with the optical transition matrix elements and band bending due to built-in electric fields (see below) in determining the band offset from the emission spectra. Similar ''apparent'' band offsets of about 2–3 meV are also obtained from the other two samples showing PLU. In contrast, the magnetic-field dependence of the ~1.49-eV transition measured in sample S1 is characteristic of the well-known donor-acceptor transition in GaAs (Ref. 9) and therefore this sample is expected to have a type-I alignment.

To show conclusively that a type-II band alignment is necessary for the up-conversion of PL at the GaAs/$GaInP_2$ heterojunction, we applied hydrostatic pressure to sample S1. It is well established that pressure tends to increase the energy gap between the *s*-like conduction-band minimum and the *p*-like valence-band maxima at the Brillouin-zone center in zinc-blende-type semiconductors.[10] Since the pressure coefficient of the GaAs gap[11] (115 meV/GPa) is much larger than the corresponding coefficient of 76 meV/GPa in partially ordered $GaInP_2$ (Ref. 12) one expects that hydrostatic pressure will raise the GaAs conduction band relative to that of $Ga_xIn_{1-x}P$ thus converting a type-I conduction alignment to type II at a sufficiently high pressure. When this occurs PLU will be ''turned on'' if the TS-TPA mechanism is correct. Indeed we observe a *pressure-induced PLU* in S1 at a pressure of 1.2 GPa (see Fig. 4). Furthermore, we notice that a new structure *lower* in energy than the donor-acceptor transition by about 4 meV has appeared. This can be explained by a spatially indirect transition between an electron in $GaInP_2$ and an acceptor in GaAs as in T700. A more definitive identification requires the simultaneous application of both pressure and magnetic field, a project we intend to carry out in the near future. However, since this experiment has been reproduced on different pieces of the sample S1, it is clear that a type-II band alignment has been achieved in S1 which makes PLU possible.

The TS-TPA process discussed in this paper and in Ref. 5 is different from previously studied TS-TPA mechanisms such as in Ref. 6. In those mechanisms, all the transitions occur within the same material. This greatly limits the flexibility in utilizing this phenomenon in applications. For example, in type-I quantum wells, the one-photon absorption process and the lifetime of the intermediate state is determined completely by the localized excitons. In the present model, the one-photon excited electrons and holes are separated spatially across a type-II interface. The electron-hole pair lifetime and PLU efficiency can be controlled by the band bending at the interface. Before concluding, we should point out that a piezoelectric field is produced by the CuPt ordering of $GaInP_2$. Recently, the existence of this electric field has been demonstrated both theoretically[3] and experimentally.[13,14] In a partially ordered and single-variant sample, this field has been determined to be 32 mV/nm pointing away from the GaAs substrate towards the $GaInP_2$[14] Thus this ordering induced field helps to propel the hole excited in the second absorption step into $GaInP_2$ while keeping the electrons localized near the type-II interface. One consequence of this is that the free electrons contributing to the PLU should form a two-dimensional gas at the interface.

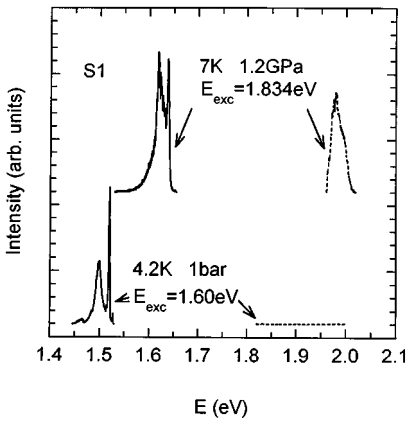

FIG. 4. A comparison between the emission spectra of S1 measured at 1 bar and at 1.2 GPa. The up-converted spectra are represented by broken curves. Notice that the GaAs emission peaks are shifted to higher energy by pressure.

In conclusion, we have studied the up-conversion of photoluminescence in a series of GaAs/(ordered)$GaInP_2$ heterojunctions using high magnetic field and high pressure. The magnetic-field dependence of the upconverted PL spectra shows that they involve a recombination of localized and free carriers. All samples exhibiting PLU at ambient pressure have a type-II band alignment. On the other hand, a sample which does not show PLU as a result of type-I alignment has been ''pressured'' to do so by converting its alignment into type II. Thus a two-step two-photon absorption process occurring at a type-II interface and possibly assisted by an built-in electric field is the key to understanding the efficient PLU at the GaAs/(ordered)$GaInP_2$ heterojunctions.

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