LBNL-39427
UC-404

CONF-960781--9

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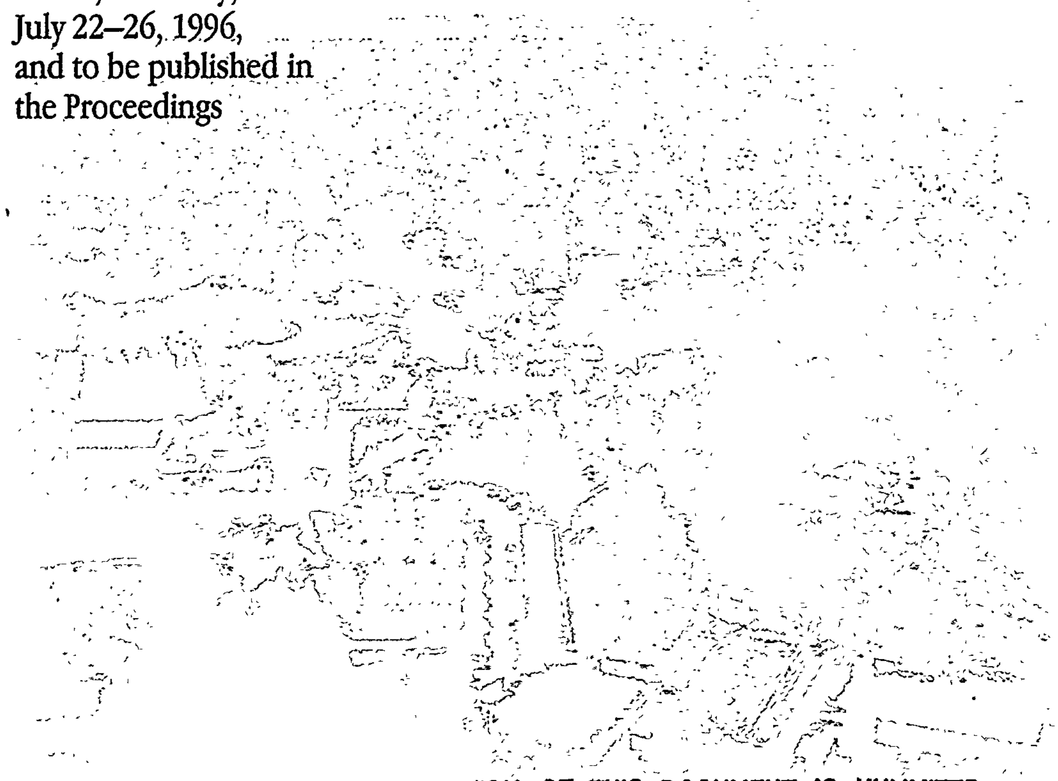
September 1996
Presented at the
23rd International Conference on the Physics of Semiconductors,
Berlin, Germany,
July 22–26, 1996,
and to be published in
the Proceedings



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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

UPCONVERSION OF NEAR GaAs BANDGAP PHOTONS TO $GaInP_2$ EMISSION AT THE GaAs/ (ordered) $GaInP_2$ HETEROJUNCTION

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We have observed upconversion of photoluminescence in several partially ordered $GaInP_2$ epilayers grown on [100] oriented GaAs substrates. We found that this upconversion occurs even when the excitation photon energy is *below* the bandgap of GaAs but near the electron-acceptor transitions at ~1.49 eV. A two-step two-photon absorption model in which the conduction band alignment at the GaAs/ $GaInP_2$ is of type II is proposed to explain our results.

$GaInP_2$ grown on GaAs substrates under appropriate conditions is known to form naturally ordered superlattices with the CuPt structure.[1] Although the interface plays an important role in the formation of the ordered structure, little is known about it due to difficulties in probing the heterojunction in as grown samples. It has been reported recently by Driessen[2] that emission from $GaInP_2$ at 1.90 eV can be excited by photons with energy slightly above the bandgap of GaAs near 1.51 eV in GaAs/$GaInP_2$ quantum wells. Since this upconversion process occurs in the vicinity of the interface, it can be used to probe properties of the heterojunction such as the band offsets and diffusion of carriers across the interface. We have studied the upconversion of photoluminescence (PL) in a simpler system containing only one GaAs/$GaInP_2$ interface. A two-photon absorption (TPA) mechanism is proposed to explain our results.

Our samples were grown by MOCVD on exactly [001] oriented semi-insulating GaAs substrates. The degree of ordering in the $GaInP_2$ epilayers was varied by setting the growth temperatures at 650, 700 and 750 °C. "Normal" and "upconverted" PL spectra were excited, respectively, by an Ar ion laser and a tunable cw Ti:sapphire laser (average power < 300 W/cm^2). All measurements were

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performed at a temperature of 10 K. We shall focus on the sample grown at 700 °C (designated as T700) only as it shows the highest upconverted PL intensity.

Figure 1 shows a comparison of the "normal" and the "upconverted" PL spectra in sample T700 excited by the Ar laser and Ti:sapphire laser, respectively. The normal PL spectrum shows an excitonic peak at 1.899 eV. The upconverted PL spectra can be deconvoluted into three Gaussian peaks (labeled as 1, 2 and 3). We also observed PL from the underlying GaAs epilayer. The sharp peaks at 1.514 eV and 1.517 eV can be attributed, respectively, to bound- and free-exciton recombination in GaAs. The broader structure at 1.496 eV can be resolved into two peak peaks as shown in Fig.1. With the help of high magnetic field[3] the higher energy peak has been identified with recombination of an electron (e) in GaAs with an acceptor A in GaAs while the lower energy peak can be attributed to a *spatially indirect* transition of an electron in $GaInP_2$ with acceptor A in GaAs.

We have studied the upconverted PL spectra as a function of excitation photon energy as shown in Fig. 2. The excitation spectra for peaks 2 and 3 are different below the exciton and bandgap of GaAs. Peak 3 shows an onset at 1.492 eV which is absent for peak 1 and peak 2. The excitation spectra of all three peaks plotted on a log scale in the inset show that they are strongly enhanced at the exciton and bandgap of GaAs.

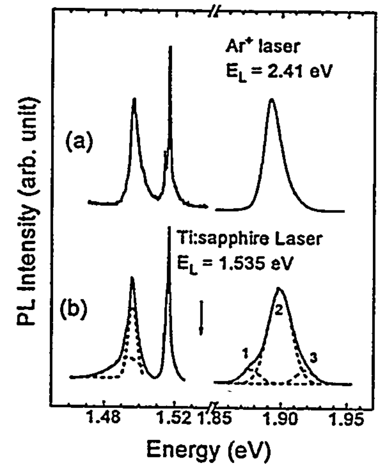

Figure 1: PL spectra excited with (a) Ar laser (2.41 eV) and (b) Ti:sapphire laser (1.535 eV). See text for assignment of peaks.

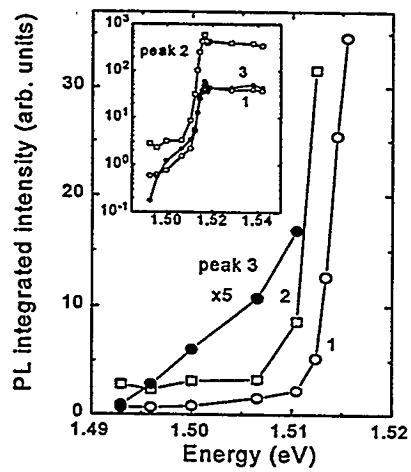

Figure 2: Integrated intensities of the upconverted PL peaks as a function of laser photon energy. The number 1,2, and 3 refer to the three deconvoluted peaks shown in Fig. 1(b). The inset shows their intensities on a log scale.

To understand our results we propose a two-step TPA mechanism[4] in which two photons are *sequentially* absorbed in combination with a type II conduction band alignment as shown in Fig. 3. The conduction band offset of 3 meV was determined by Zeman *et al.*[3] in the same sample. In this model the electron excited by the first photon diffuses spontaneously into $GaInP_2$ without the assistance of a second photon. The electron and hole lifetimes are lengthened by their spatial separation allowing a second photon to excite the hole across the ~0.4 eV barrier between the GaAs and $GaInP_2$ valence bands.

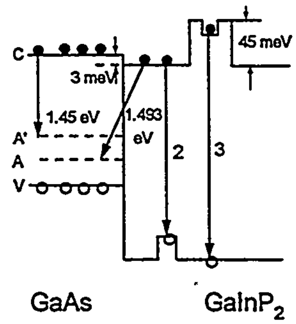

Figure 3: Schematic model to explain PL upconversion at the GaAs/$GaInP_2$ interface. C, A, A' and V denote, respectively, the conduction band edge, shallow and deep acceptors, and valence band edge. Arrows labeled 2 and 3 correspond to the upconverted PL peaks 2 and 3 in Figs. 1(b) and 2.

With this model it is easy to understand why upconverted PL can be observed even when the excitation photon energy is below the band gap of GaAs since elecrons can be excited from both the valence band and the shallow acceptors A in GaAs to the conduction band in $GaInP_2$. However, this model cannot explain why the onset at 1.492 eV was observed only in the excitation spectrum of peak 3. In fact Zeman *et al.*[3] have found, via high-magnetic-field measurements, that the upconverted $GaInP_2$ PL peaks involved either localized holes (peak 2 in Figs. 1 and 2 and transition labeled 2 in Fig. 3) or localized electrons (peak 3 and transition 3 in Fig. 3). The localization of electrons and holes is necessary to prevent their "backflow" from the $GaInP_2$ to the GaAs as pointed out by Driessen.[2] In the case of peak 3, Zeman *et al.*[3] found that the electrons are trapped in a *metastable* localized state with energy about 18 meV *above* the $GaInP_2$ conduction band edge. This implies that the onset for exciting electrons from acceptors into $GaInP_2$ to produce peak 3 has to be higher than for peak 2 by at least 18 meV. This suggests that it will take at least 1.511(=1.493+0.018) eV of energy to excite an electron from A into the localized electron level in $GaInP_2$. Thus we have to invoke another acceptor (A') whose binding energy is larger than A to explain the onset at 1.492 eV for peak 3. A transition at 1.45 eV have indeed been observed in sample T700 under laser excitation with photon energies < 1.486 eV. For higher photon energies this peak is obscured by the longitudinal optical phonon sideband of the dominant electron (e)-A transition. If we interpret this peak as due to an e-A' transition in GaAs then from the energies of 1.492 eV for the onset, 1.45 eV for the e-A' transition and 3 meV for the conduction band offset we deduce an energy of ~45 meV for the barrier height of the metastable localized electron trap. The contribution of A' to upconversion in spite of the weak emission intensity of the e-A' transition suggests that A' is probably located very close to the $GaInP_2$/GaAs heterojunction.

Driessen[2] has invoked the "cold Auger mechanism" to explain his upconversion results in GaAs/$GaInP_2$ quantum wells. However, we found it difficult to explain many of our results with this mechanism, such as the difference in onset behavior between peaks 2 and 3, and the possibility of exciting upconverted PL via acceptors in GaAs. For Auger mechanism to occur at acceptors one has to assume either that these are double acceptors or that there is overlap between the hole wave functions on different acceptors to form acceptor bands. The acceptor concentration in our sample ($<10^{16}$ cm^{-3}) is not high enough to form acceptor bands.

In conclusion, we found that a two-step TPA mechanism based on a type II conduction band alignment at the GaAs/$GaInP_2$ interface not only explain the strong upconversion efficiency observed at partially ordered $GaInP_2$ grown on GaAs but also features of the upconversion excitation spectra at photon energies below the bandgap of GaAs.

Acknowledgments: This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098. KLT acknowledges a fellowship from the National University of Singapore while PYY acknowledges a fellowship from the J. S. Guggenheim Memorial Foundation. We are grateful to J. Zeman and G. Martinez for making available to us their high magnetic field results before publication.

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