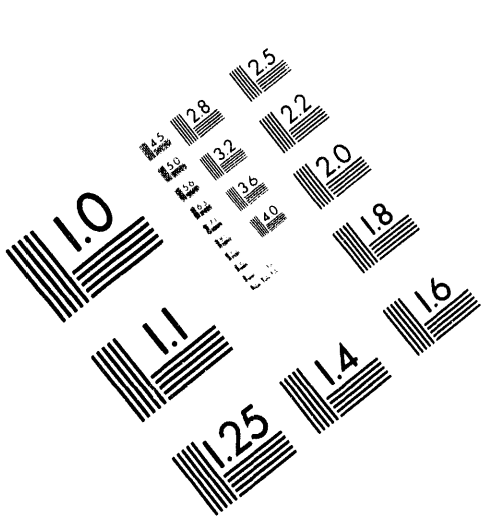

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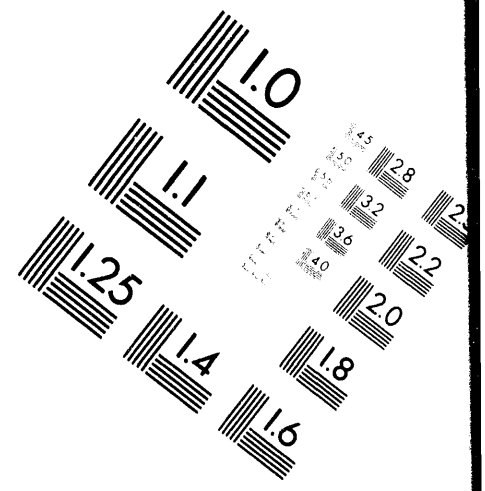

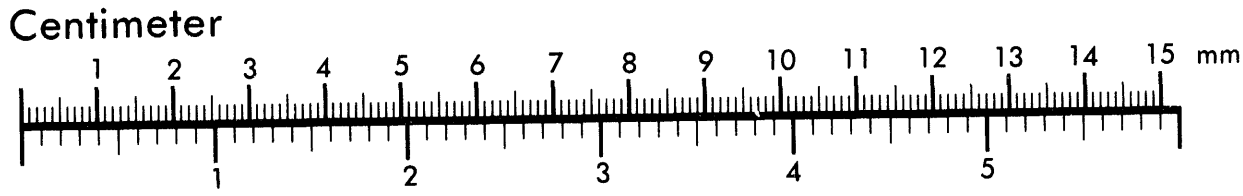

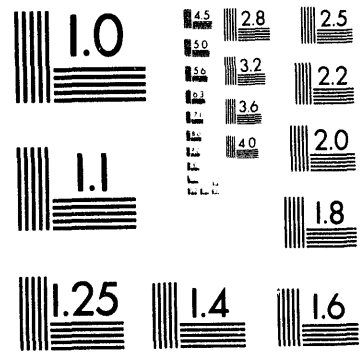

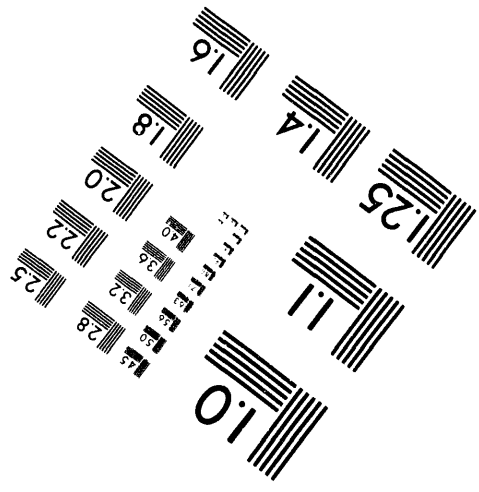

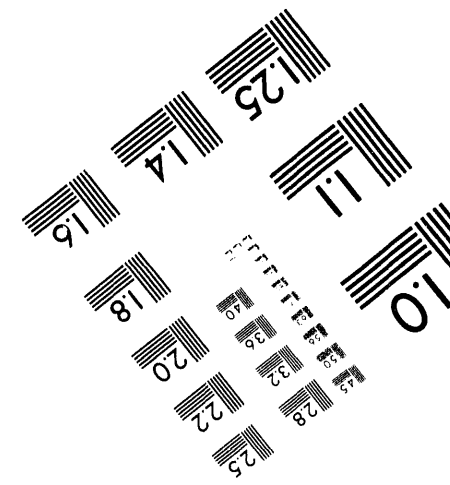

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OBSERVATION OF EXITONIC AND BAND-TO-BAND BEHAVIOR IN ORDERED $InGaP_2$ ALLOYS

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ABSTRACT

Photoluminescence measurements on ordered $InGaP_2$ were studied as a function of temperature, laser power density, and magnetic field. The temperature varied between 1.4 and 300 K, the laser power densities ranged from 10 nW/cm^2 to 20 W/cm^2, and the maximum magnetic field was 13.6 T. The data show both excitonic and band-to-band behavior, depending upon the incident laser power density. A consistent interpretation of all data leads to a type-II valence-band offset between the ordered domains.

The $In_xGa_{1-x}P$ alloy system exhibits many interesting physical properties. For concentrations x ~ 0.5, there are several crystallographic phases, varying from an disordered alloy, with the zincblende structure, to an ordered CuPt-type structure. Concomitant with the differing crystallographic forms is a changing bandgap energy. The reader is referred to two recent review articles,[1,2] and the references therein, describing some of the physical properties of this material system. Coincidently, the lattice constant for $InGaP_2$ is nearly equal to that of GaAs; thus there have been many studies describing the differences in the optical properties, bandgap energies, etc., between the disordered and CuPt-type ordered phases of $InGaP_2$. Because of the large numbers of reported photoluminescence (PL) studies only a few recent publications describing these observations[3-7] are referenced here and this list is not meant to be complete.

In this paper, we report on temperature and magnetic field dependent PL studies of an $InGaP_2$ alloy lattice-matched to GaAs which exhibits well behaved ordering properties, i.e., a narrow range of order parameters. The sample (#XD0413A - $In_{0.48}Ga_{0.52}P$/GaAs) was grown at a temperature of 675 C by low-pressure metal-organic chemical vapor deposition on a (100) GaAs substrate, tilted 2° towards <110>. Room temperature sample characterization techniques consisted of double-crystal x-ray scattering measurements, transmission electron microscopy measurements, polarized photomodulated reflectance spectroscopy, and ellipsometry. The double-crystal x-ray scattering data show that the $InGaP_2$ lattice constant is within 0.1% of the GaAs-substrate lattice constant. The results from the transmission electron microscopy measurements show that there is almost a single <111> variant for the CuPt-type ordering. Analyses of the polarized photomodulated reflectance spectroscopy indicate that the energy difference between the crystal field split valence-bands is about 30 meV.

Temperature dependent PL measurements were made between 1.4 and 300 K. Figure 1 shows 4-K spectra taken at two different laser power densities, 60 nW/cm^2 and 4 W/cm^2.

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The peak of the 4 W/cm^2 spectrum is near 1900 meV while the 60 nW/cm^2 spectrum has two peaks, a smaller amplitude still at 1900 meV and the other (largest) near 1840 meV. The peak-amplitude of the of the 4 W/cm^2 data is about 1000 times larger than that for the

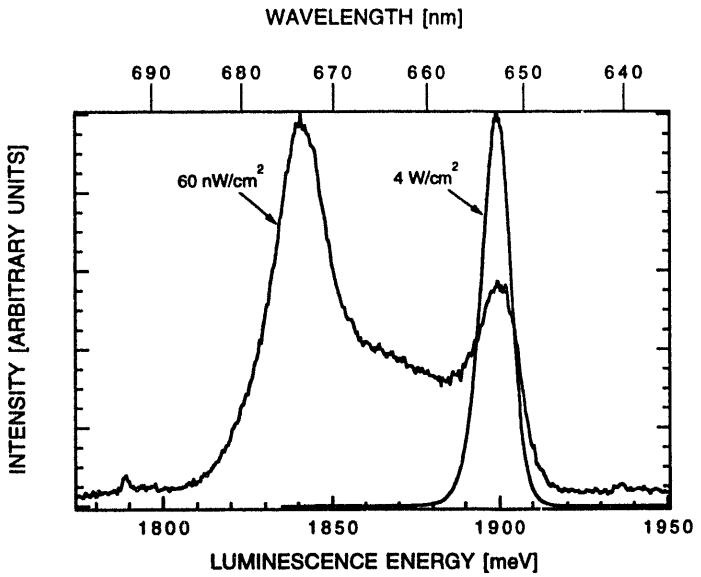

FIG 1. Low temperature (~ 4 K) photoluminescence spectra at two laser power densities, 60 nW/cm^2 and 4 W/cm^2. The peak amplitude for the higher power density is about 1000 times larger than the peak amplitude of the lower power density spectrum.

60 nW/cm^2 spectrum. As can be seen in Fig. 1, there is still evidence of a peak near 1900 meV for the low power density data and a detailed examination of the high power density data shows a small-amplitude peak near 1850 meV. Thus, depending on the incident power density of the exciting laser, the peak appears to move between 1840 and 1900 meV. Power dependent shifts for ordered $InGaP_2$ alloys the have been previously studied by DeLong et al[3] and they presented their results in terms of a spatially indirect conduction electron and a valence-band hole. We performed low-temperature PL lifetime time measurements as a function of energy on our sample and find, in agreement with others[3,6], that for the low energy portion of the spectrum, the PL decay time τ is very long, τ ~ 50μsec while for the high energy side of the spectrum (e.g., E ~ 1900 meV) τ < 100 nsec, the resolution of our measurement.

The temperature dependencies of the spectra shown in Fig. 1 were also studied between 1.4 and 300 K and again there are observed spectral peak shifts and our observations are in substantial agreement with similar studies.[3,5] The main result of these studies is that as the temperature is raised from 4 K, the double peak structure disappears leaving only the single higher energy peak identical to that in the higher power density data.

In order to gather new information about the mechanisms giving rise to the spectra shown in Fig. 1, we performed magnetoluminescence measurements between 0 and 14 tesla. The orientation of the applied magnetic field was along the growth direction, e.g., (100) and hence the field is at an angle to the (111) ordering planes. From the magnetic field dependence of the PL shift, one can distinguish between excitonic behavior, band-to-band transitions, or donor-acceptor pair recombination. The diamagnetic energy shift for an exciton is given by

$$\Delta E_{ex}^{dia} = \frac{\hbar^4 \kappa^2}{4\mu^3 e^2 c^2} B^2, \qquad (1)$$

where B is the magnetic field, μ is the reduced mass ($\mu^{-1} = m_c^{-1} + m_v^{-1}$) where m_c and m_v are respectively the conduction-band and valence-band effective masses in terms of the free electron mass m_0, and κ is the dielectric constant.

The magnetic field dependence of the higher laser power density data of Fig. 1 is shown as the lower data set in Fig. 2. The solid line drawn through the data is quadratic, i.e., $\Delta E \sim B^2$, indicating excitonic behavior. Using a conduction band mass $m_c \sim 0.1 m_0$ and a valence band mass $m_v \sim 0.2 m_0$ yields reasonable agreement between (1) and the measured energy shift. It should be noted here that for disordered $InGaP_2$ alloys, an analysis of the magnetic field induced shifts also indicated[4] excitonic behavior, i.e., $\Delta E \sim B^2$.

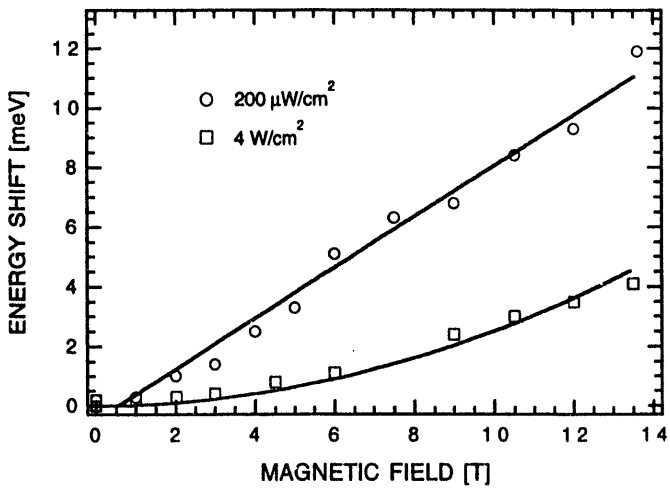

FIG 2. Magnetic field induced PL shifts at 1.4 K for two laser power densities, 200 $\mu W/cm^2$ ($E_{peak} \sim 1850$ meV) and 4 W/cm^2 ($E_{peak} \sim 1900$ meV). The straight line drawn through the 200 $\mu W/cm^2$ data has a slope of 0.87 meV/T. An analysis of the higher power density (4 W/cm^2) data shows that the "best fit" function is quadratic in the magnetic field.

Low-temperature polarized photoluminescence excitation (PLE) spectroscopy measurements were also made on this sample and the peak in the PLE was found to be at about 1915 meV, or in other words, a binding energy of about 15 meV can be ascribed to the high power density peak (excitonic) peak. For excitons in $InGaP_2$ the expected Rydberg is in the same range (15 meV) which along with the quadratic field dependence and short PL decay times confirm the excitonic identification for this PL peak.

In contrast to the quadratic field dependence of (1), band-to-band luminescence energy shifts are linear in the magnetic field and given by

$$\Delta E_{bb} = \left(n + \frac{1}{2}\right)\frac{e\hbar B}{\mu c}, \qquad (2)$$

where n = 0, 1, 2, 3 ... is the Landau index.

The linear field dependence of low power density data (Fig. 2) is interpreted here as band-to-band behavior. The maximum energy shift of 12 meV is fairly large and is also indicative of the band-to-band nature of this peak. Magnetic field induced energy shifts were also taken for a range of other power densities between those shown in Fig. 2 with the result that as the power-dependent peak-intensity neared the exciton peak, the magnitude of the maximum shifts were reduced and the magnetic dependence went from linear behavior at low power densities to quadratic at high power densities.

Because of this linear field behavior, we believe that the PL peak found for low power densities represents a band-to-band transition. Using (2) and the measured slope of 0.85 meV/T, one can calculate the reduced mass μ. Furthermore, the conduction-band mass in

ordered $InGaP_2$ was recently measured[8] to be $m_c \sim 0.09m_0$ by cyclotron resonance techniques. With a knowledge of the reduced mass μ from (2) and the conduction-band mass m_c from the cyclotron resonance measurement, the valence-band mass m_v can be inferred to be $m_v \sim 0.25m_0$. Using the measured crystal-field split valence-band energy of 30 meV, we have performed a *k•p* calculation for ordered $InGaP_2$ and find that the valence-band is highly anisotropic, with $m_v$varying from $0.16m_0$ in the (111) plane to $0.33m_0$ for a direction perpendicular to (111). For a magnetic field along the (100) direction, the *k•p* calculation yields a valence-band mass $m_v \sim 0.2m_0$ which is in good agreement with that inferred ($0.25m_0$) from the magnetoluminescence data. Because of the linear magnetic field shift for the low power density PL peak and the agreement for the calculated and inferred valence-band masses, we assign these transitions as band-to-band.

The long lifetimes and linear magnetic field dependent energy shifts for the low power density data suggest a spatially indirect electron-hole recombination process. We rule out donor to acceptor recombination based on two reasons; (1) the magnetic field data yielded a valence band mass of $m_v \sim 0.25m_0$ in agreement with theoretical expectations, and (2) for donor-to-acceptor transitions the acceptor masses are very heavy and hence, the inferred mass would be $m_v > 0.7m_0$.

Both DeLong et al[3] and Fouquet et al[6] suggest that spatially indirect electron-hole recombination is a result of radiative transitions in a disordered matrix of $InGaP_2$ containing the CuPt-type ordered $InGaP_2$, i.e., "concrete." On the other hand, Horner et al[7], present a picture where there is no disordered phase in the sample, but where all observations can be explained by considering a distribution function for the order parameter.

All of our data resulting from PL, PLE, photomodulated spectroscopy, or ellipsometry measurements show no indication of bandgap absorption near 2 eV, where the disordered phase of $InGaP_2$ should appear. In order to present a consistent interpretation of the data in terms of the model presented by Horner et al,[7] we have to postulate a type-II valence-band offset. A type-II valence-band offset between ordered domains with differing order parameters is unexpected and theoretical calculations for the offset are being pursued.

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