Low-temperature cleaved-edge polarized-photoluminescence studies of spontaneously ordered $GaInP_2$ alloys

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We report low-temperature polarized-photoluminescence (PL) measurements on (110) cleaved edges of ordered GaInP$_2$ alloys. By comparing the intensity of the forbidden PL polarized along the ordering axis with that of the allowed PL polarized orthogonal to the ordering axis, we study the effect of coulomb interaction on the excitonic transition rate. The experimentally obtained polarization ratios of 13–20 are consistent with calculations based on an eight-band **k·p** model. © *1998 American Institute of Physics.* [S0021-8979(98)08903-8]

Spontaneous CuPt$_B$-type long-range ordering in GaInP$_2$ has been a subject of intense studies in recent years.[1] Ga$_x$In$_{1-x}$P ($x \cong 0.52$; written as GaInP$_2$ for simplicity in this paper), grown lattice-matched to a (001) GaAs substrate by organometallic vapor phase epitaxy (OMVPE), exhibits ordering of the cations on the group-III sublattice depending on the growth conditions and the substrate misorientation. The ordered alloy consists of a monolayer superlattice of Ga$_{1+\eta}$In$_{1-\eta}$P$_2$/Ga$_{1-\eta}$In$_{1+\eta}$P$_2$ along $[\bar{1}11]$ or $[1\bar{1}1]$, which are the two $[111]_B$ directions, where the order parameter η ranges from 0 to 1. When the ordering is single variant, i.e., the ordering occurs along only one of the two $[111]_B$ directions throughout the sample, this structure has trigonal symmetry with point group C_{3v}, while the random alloy of GaInP$_2$ has the cubic zinc-blende structure with point group T_d.

The ordering-induced reduction in symmetry removes the fourfold degeneracy at the valence-band maximum (**k** $=0$) of the zinc-blende random alloy, and leaves doubly degenerate states $|v_{1,2}\rangle = |J=3/2, m_{z'}=\pm 3/2\rangle$ as the topmost valence-band states. (We choose the ordering direction $[\bar{1}11]$ as the z' direction.) It is well known that the optical transition between the $|v_{1,2}\rangle$ states and the s-like conduction-band states $|c_{1,2}\rangle$ is dipole forbidden if the light is polarized along the z' direction.[2] This selection rule has been employed in a room-temperature polarized luminescence study from the cleaved edge to estimate the valence band splitting in ordered GaInP$_2$.[3] However, this selection rule is strictly valid only for the band-to-band transition at the band edge (i.e., **k**$=0$). In reality, in absorption, reflectance, or low-temperature luminescence measurements, excitonic, rather than the band-to-band, transitions are involved. For the exciton states, the Coulomb interaction couples $k \neq 0$ states as well as the states of the nearby bands. Thus, the exciton ground state associated with the topmost valence band does not preserve the $|3/2, \pm 3/2\rangle$ symmetry, but rather mixes with other nearby band edge states $|v_{3,4}\rangle = |3/2, \pm 1/2\rangle$ and $|v_{5,6}\rangle = |1/2, \pm 1/2\rangle$, as well as the $k \neq 0$ states. As a result, the selection rule is relaxed and the forbidden transition becomes partially allowed.

However, the excitonic effects are usually ignored either

in analyzing various types of polarized spectra (e.g., piezo-modulated reflectance,[4] reflectance difference,[5] or electroreflectance[6] spectroscopies) or in theoretical studies[7–9] of the optical polarization in ordered alloys. In a recent study of the luminescence polarization in ordered GaInP$_2$, it was pointed out that the excitonic effects can significantly modify the optical polarization predicted by the simple band-to-band transition model.[10] In this work, it was shown that the ratio of the optical transition intensity with polarization along the $[110]$ (or equivalently $[1\bar{1}2]$) direction to that along the $[\bar{1}11]$ direction changes from infinity for the band-to-band transition to ~ 10 when the excitonic effect is taken into account. However, since most polarized spectroscopy measurements are performed on the $[001]$ growth surface, a direct comparison of this prediction and experimental data has not been possible. Since controlling the polarization of the luminescence is an important part of designing lasers based on GaInP$_2$, understanding the excitonic effects on the polarization will be important in optimizing the laser performance.[11] In this letter, we present the result of our low-temperature polarized photoluminescence (PL) study on the $[110]$ cleaved edge of ordered GaInP$_2$ samples, and compare the results with calculations to elucidate the effect of the excitonic interaction on the selection rule of optical transitions.

We present results for four samples whose PL spectra showed an excitonic peak that is well resolved from the defect-related below-gap luminescence peak. These samples have a 10 μm thick GaInP$_2$ epilayer grown by OMVPE on a (001) GaAs substrate. The substrate misorientation, the growth temperature, the growth rate, and the V/III ratio were varied to obtain different degrees of ordering. The growth parameters of the samples are summarized in Table I, along with their band-gap energies as determined by PL excitation measurements on the [001] surface. The substrate misorientation toward $[\bar{1}11]$ results in single variant ordering.[12] The sample was mounted on a cold finger of an Oxford Microstat helium cryostat with a 500 μm thick window, and the PL measurements were taken on the (110) cleaved edge at 4.2 K. The 5145 Å line of an Ar ion laser was used as the excitation source. About 5 μW of the laser was focused with an all-mirror microscope objective (NA$=0.5$) to a spot size of approximately 2 μm, which is much smaller than the thickness of the GaInP$_2$ layer. The laser was focused near the center of

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TABLE I. Sample growth parameters and measured polarization ratios.

Sample	T_g (°C)	Substrate	x	E_g (eV)	R
1	680	6° $[\bar{1}11]_B$, Cr doped	0.516	1.907	15.9
2	690	6° $[\bar{1}11]_B$, Si doped	0.522	1.927	20.1
3	690	4° $[\bar{1}11]_B$, Si doped	0.522	1.924	13.1
4	690	6° $[\bar{1}11]_B$, Cr doped	0.521	1.929	14.5

the GaInP$_2$ layer in order to avoid waveguide effects due to the GaAs/GaInP$_2$ interface and the surface. The PL signal was collected by the same objective, dispersed by a SPEX 1877 0.6 m triple spectrometer, and detected with a high-resolution charge-coupled device detector array. A linear polarizer was used to analyze the polarization of the luminescence, and a half-wave retarder was used to ensure that the light entering the spectrometer is always polarized in the same orientation. The substrate misorientation was taken into account in aligning the polarizer. In order to test the possibility of the polarization-dependent throughput of the optical setup, we measured the luminescence from the GaAs substrate of the samples and no polarization of the GaAs luminescence was observed.

Figure 1 is a comparison of two PL spectra of sample 1 for polarizations along the two principal axes of the ordered alloy, $z' = [\bar{1}11]$ and $x' = [1\bar{1}2]$. In the x'-polarization spectrum, the sharp peak at 1.900 ± 0.001 eV is due to the intrinsic excitonic transitions[13] and the broad peak at ~ 1.87 eV is due to defect-related transitions. In the z'-polarized spectrum, the excitonic peak is very weak but finite, while the low-energy peak is weaker than the x'-polarization case by $\sim 50\%$. In order to obtain the polarization ratio $R = I^{x'}/I^{z'}$, where I^e is the intensity of the excitonic PL polarized along the $\mathbf{e}$ direction, the spectra were fitted with multiple Gaussian curves (single Gaussian for the excitonic peak) and the inte-
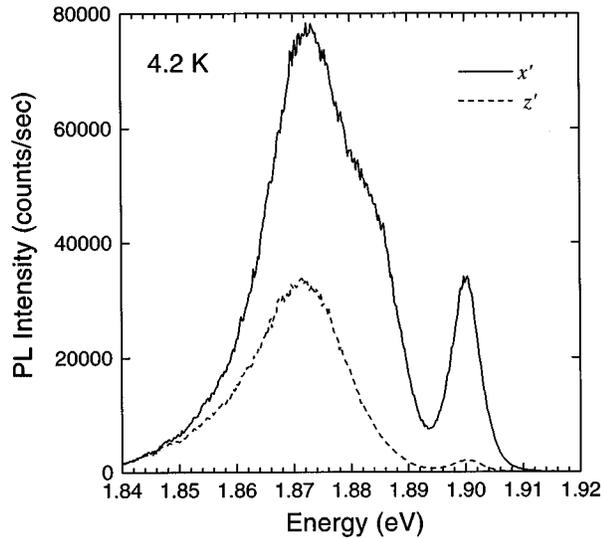
grated intensity of the excitonic peak was obtained. The R values thus obtained for the four samples are summarized in Table I.

The optical transition matrix element for an excitonic state at $\mathbf{k}_{ex} = 0$ is given by[14]

$$M_{ex}(k_{ex} = 0, \mathbf{e}) = \sum_{\mathbf{k}} A(\mathbf{k}) M_{cv}(\mathbf{k}, \mathbf{e}), \qquad (1)$$

where $M_{cv}(\mathbf{k}, \mathbf{e}) = \langle \varphi_c(\mathbf{k}) | \mathbf{e} \cdot \mathbf{p} | \varphi_v(\mathbf{k}) \rangle$ is the matrix element for the direct *band-to-band* transition, $\mathbf{p}$ the momentum operator, $\mathbf{e}$ the polarization of the light, and $A(\mathbf{k})$ the Fourier transform of the ground-state exciton wavefunction $F_1(\mathbf{x})$. The exciton recombination rate is proportional to the square of the matrix element defined by Eq. (1). Usually, one assumes that $M_{cv}(\mathbf{k}, \mathbf{e})$ is a smooth function of $\mathbf{k}$, and obtains

$$|M_{ex}(k_{ex} = 0, \mathbf{e})|^2 \approx |M_{cv}(0, \mathbf{e})|^2 |F_1(0)|^2. \qquad (2)$$

This approximation works reasonably well unless $M_{cv}(0, \mathbf{e}) = 0$, which is the case for the transition with the z' polarization. In this case, a more sophisticated calculation is needed in order to estimate the excitonic recombination rate. In this work, we calculated the R values for ordered GaInP$_2$ alloys as a function of the degree of ordering using the formalism described in Ref. 10. In our calculation, the matrix element $M_{ex}(0, \mathbf{e})$ is numerically evaluated, with the matrix element $M_{cv}(\mathbf{k}, \mathbf{e})$ obtained using an eight-band $\mathbf{k} \cdot \mathbf{p}$ model.[15] We also considered the dependence of the calculated excitonic effect on the band-structure parameters and the deviation of the alloy composition from its lattice-matched value ($x = x_0 = 0.52$ at 4.2 K).

The calculated polarization ratio is plotted in Fig. 2 as a function of the crystal-field-splitting parameter Δ_{CF} and the band-gap energy E_g. Δ_{CF} is a quadratic function of the order parameter η $[\Delta_{CF}(\eta) = \eta^2 \Delta_{CF}(1)]$,[16] and is related to the band-gap energy by[17]

$$E_g(\eta) = E_g(0) - 2.66 \Delta_{CF}(\eta) \qquad (3)$$

for $x = x_0$. We repeated the calculation for two sets of Luttinger parameters[15,18] and a range of composition slightly deviating from $x = x_0$. Table II summarizes the band parameters used in the calculations. Also plotted in Fig. 2 are the experimentally measured R values as a function of the band-gap energy as measured by PL excitation measurements. In Fig. 2, the bottom (E_g) and the top (Δ_{CF}) abscissas are scaled according to Eq. (3). It should be noted that this scaling is only approximate for the experimental data because there is no exact one-to-one correlation between the two scales due to a slight variation of the actual composition of the samples. The experimental R values are consistent with

FIG. 1. Polarized PL spectra of sample 1 for polarizations along the z' and x' directions. The peak at $\sim 1.900 \pm 0.001$ eV is the excitonic peak.
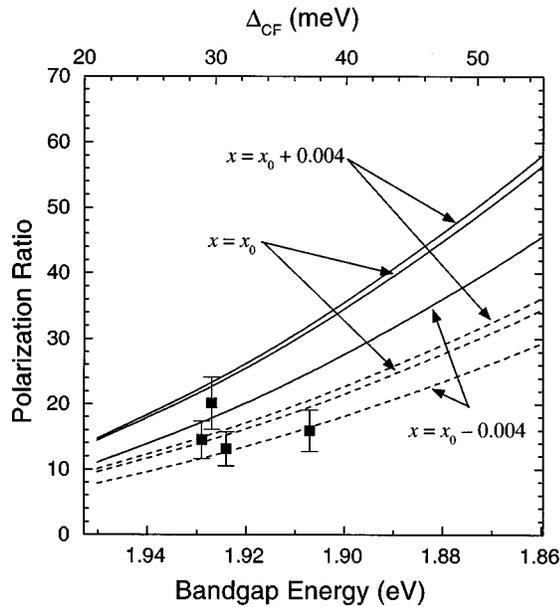
FIG. 2. Comparison of the measured and calculated polarization ratios. The solid curves are calculations with the band parameters used in Ref. 15 and the dashed curves with those used in Ref. 18. The calculations were repeated for three different compositions $x = x_0 = 0.52$, and $x_0 \pm 0.004$.

the calculated curves, and appear to be in better agreement with the curves using the parameters of Ref. 18. This agreement is especially remarkable when one considers the fact that for the band-to-band transition without the excitonic effect, the R value would be infinity.

Other factors that could also reduce the R values are defects in the samples. Because the defects reduce the symmetry of the crystal, the forbidden z'-polarized band-to-band transitions become partially allowed in the presence of the imperfections, thus reducing the R values. In fact, we measured several other samples with similar band-gap energies but with excitonic peaks that were not well resolved from the defect-related low-energy peaks, and obtained smaller R values (7–9) for those samples. Although the reduction of the R values due to the presence of defects is difficult to quantify,

the previous polarized PL study on the [001] growth surface showed that the sample-to-sample variation of the polarization ratio, which can be attributed to the presence of defects, was less than 10%.[10] For the samples presented in this communication, the excitonic peaks are well resolved from the defect peaks, and therefore we believe that the influence of defects on the R values should be very small. Another factor that could affect the polarization is mixing of states due to fluctuation in the alloy composition or the order parameter. However, this type of fluctuation potential is usually slowly varying and the effect is expected to be small.

In summary, we have studied low-temperature polarized PL on cleaved edges of ordered GaInP$_2$ alloys. The measured polarization ratios between forbidden and allowed transitions are 13–20. These measured values can be explained by the excitonic effect on the forbidden transitions and are consistent with our eight-band k·p model calculations of the excitonic recombination rates.

[1] For a review of recent progress in this field, see A. Zunger and S. Mahajan, in ''Materials, Properties and Preparation,'' edited by S. Mahajan, Vol. 3B of *Handbook on Semiconductors*, 2nd ed., T. S. Moss, series editor (North-Holland, Amsterdam, 1994), p. 1399.

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[13] By ''intrinsic,'' we mean that an exciton is not bound to an impurity or a defect. However, an exciton in an alloy may be weakly localized due to alloy fluctuation or order parameter fluctuation.

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TABLE II. Band structure parameters for Ga$_x$In$_{1-x}$P ($x \sim 0.5$).

	E_p (eV)	γ_1[a]	γ_2[a]	γ_3[a]
Ref. 15	26	0.316	-1.084	-0.626
Ref. 18	21.31	1.136	-0.442	0.101

[a] These are the so-called modified Luttinger parameters used in the eight-band k·p calculations. [C. R. Pidgeon and R. N. Brown, Phys. Rev. **146**, 575 (1966).]