Spontaneous ordering in $GaInP_2$: A polarized-piezomodulated-reflectivity study

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Piezomodulated reflectivity is used to probe the electronic structure of $GaInP_2$ epilayers grown by organometallic chemical-vapor epitaxy on misoriented [001] GaAs substrates. The epilayers, grown at different growth temperatures using 2° and 6° misoriented substrates, exhibit various degrees of ordering. Our study provides information on the fundamental gap, crystal-field splitting, and spin-orbit splitting for temperatures ranging from 6 to 250 K.

In the past, successful control over the material parameters of ternary semiconductors, such as band gaps and lattice constants, has been achieved by altering the composition. Band-gap engineering based on composition variations and multilayer structures resulted in substantial technological advances in devices such as solid-state lasers, solar cells, and a variety of detectors. Recent studies on spontaneous ordering in ternary alloys[1-9] open the possibility of controlling the physical parameters, such as the band gap, by alternating the degree of ordering in a material with a fixed composition. For example, spontaneous ordering can be achieved by growing a ternary alloy, such as $GaInP_2$, using organometallic vapor phase epitaxy (OMVPE) or molecular-beam epitaxy (MBE).[10] Ordering in $GaInP_2$ has been studied using a variety of techniques. The temperature dependence of the energy gap E_g has been investigated by electroreflectance,[11] photoluminescence (PL),[6,11-13] and excitation photoluminescence (PLE).[8,14] However, a systematic study of E_g, the crystal-field splitting Δ_c, and the spin-orbit splitting Δ_{so} as a function of temperature and ordering parameter is not yet available in the literature. Piezomodulated reflectivity (PZR) is a technique suitable for this study because it provides sharp first derivative signatures of the relevant transitions and can be applied in a wide range of temperatures. In this paper, we report a systematic temperature study of the PZR spectra of $GaInP_2$ epilayers that exhibit various degrees of ordering.

Figure 1 shows the structure of $GaInP_2$ for ordering along the $[\bar{1}11]$ direction. Note that $(\bar{1}11)$ cation planes alternate between In and Ga in the perfectly ordered structure; thus, the structure is equivalent to a GaP/InP superlattice. In the perfectly disordered structure, the cation planes contain an equal amount of In and Ga distributed randomly. A partially disordered alloy can be described as a $Ga_{0.5+\eta/2}In_{0.5-\eta/2}P/Ga_{0.5-\eta/2}In_{0.5+\eta/2}P$ superlattice, where η defines an ordering parameter ranging from $\eta=0$ (disordered alloy) to $\eta=1$ (ordered alloy).

Ordering affects the symmetry and, thus, the physical properties of the alloy. For example, ordering in $GaInP_2$ defines a larger unit cell and thus a smaller Brillouin zone than that of the disordered zinc-blende material. The resulting folding of the L point of the disordered alloy into the zone center of the CuPt ordered alloy reduces the band gap as a result of repulsion between the upper lying folded state and the bottom of the conduction band. In addition, the lower $3m$ point-group symmetry of the ordered alloy splits the top of the valence band, which results in directionally polarized optical properties and a crystal-field splitting Δ_c that depends on the degree of ordering.[6-9] Figure 2 shows the band structure at the Γ point for disordered (space group $F\bar{4}3m$) and ordered (space group $R3m$) $GaInP_2$.[6] The relevant electronic transitions with energies E_g, $E_g+\Delta_c$, and $E_g+\Delta_{so}$ are indicated.

Table I shows the growth parameters for 11 samples obtained by atmospheric-pressure OMVPE in a vertical pancake-style reaction vessel. In the first seven samples, we use a fixed inlet V/III ratio of 50, a phosphine partial pressure of 230 Pa, a growth rate of 4.4 μm/h, and substrate misoriented 2° off the (001) plane toward the $[0\bar{1}1]$ direction, varying only the growth temperature T_g between 600 and 750 °C. The set of four subsequent samples uses a fixed but higher V/III ratio of 340, a phosphine partial pressure of 680 Pa, a fixed but lower growth rate of 1.9 μm/h, and a different substrate misorientation of $\theta_B=6°$ toward $\langle 111\rangle_B$.

The samples were grown lattice matched to the GaAs substrate. Small deviations (strain $\lesssim 2\times10^{-3}$) from the lattice-matched composition $Ga_{0.515}In_{0.485}P$ were measured using double-crystal x-ray diffraction on the (004) reflection. The various measured energies could be affected by slight deviations from the nominal composition. To correct for composition-induced changes in E_g, we first measure E_g vs lattice mismatch Δa for a set of

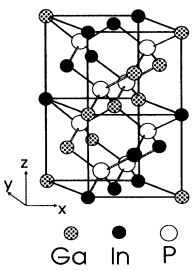

FIG. 1. Structure of perfectly ordered $GaInP_2$ for ordering along the $[\bar{1}11]$ direction.

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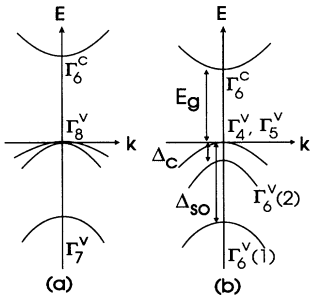

FIG. 2. Band structure at the Γ point for (a) disordered and (b) ordered $GaInP_2$.

samples of varying composition and growth temperatures. We then correct E_g by the appropriate energy shift required to produce $\Delta a = 0$ (lattice matched at room temperature).

The piezomodulated reflectivity spectrum of the crystals was accomplished by mounting the sample on a lead-zirconate-titanate transducer driven by a sinusoidal voltage at 610 Hz. The alternating expansion and contraction of the transducer subjects the sample to an alternating strain with a typical-root-mean-square value of $\sim 10^{-5}$. A helium/nitrogen transfer optical cryostat was employed for low-temperature measurements. A single grating SPEX monochromator with a tungsten halogen lamp was used as a monochromatic light source, and an uv-enhanced low-noise Si photodiode constituted the detector. In the reflectivity experiments, the incident light is polarized either parallel or perpendicular to the $[\bar{1}10]$ direction, where $[\bar{1}10]$ is the projection of the $[\bar{1}11]$ or $[1\bar{1}1]$ ordering axis on the (001) sample surface. We note that only $CuPt_B$ variants $[(\bar{1}11)$ and $(1\bar{1}1)]$ have been observed, and that the $CuPt_A$ variants $[(\bar{1}\bar{1}1)$ and $(\bar{1}11)]$ are absent in ordered $GaInP_2$.[4]

Figure 3(a) shows the piezomodulated reflectivity spectra of sample K-078 for both polarization directions at $T = 15$ K. As seen, the crystal-field splitting between the two polarization directions is very small (~ 2 meV), indicating that this is a highly disordered sample. The residual crystal-field splitting indicates that total disorder has not been achieved. In order to determine the transition energies accurately, we have performed a theoretical line-shape fitting, as shown in the inset. The functional form used in the fitting procedure corresponds to a Lorentzian $\Delta R/R = \mathrm{Re}[Ae^{i\theta}(E - E_g + i\Gamma)^{-n}]$, where A, θ, E_g, and Γ are the fitting parameters and E is the energy. For piezomodulated reflectivity (first derivative functional form), $n = 2.0$ for excitonic transitions and $n = 0.5$ for interband transitions (three-dimensional critical point).[15] Our experimental signatures are more consistent with excitonic line shapes. A least-square fit to the experimental data was achieved by using the Levenberg-Marquardt method.[16] As can be seen, the fit reproduces the observed line shapes reasonably well. The dominant feature near $E_g = 1.98$ eV (1.989 eV corrected) can be associated with the excitonic transition from the (nearly degenerate) top of the valence band to the bottom of the conduction band. The feature near 2.08 eV corresponds to the transition between the top of the spin-orbit split-off band and the bottom of the conduction band. The spectra give a spin-orbit splitting of $\Delta_{so} \approx 103$ meV at $T = 15$ K for this nearly random sample. The small dip at 1.86 eV corresponds to the spin-orbit transition of the GaAs substrate.

Figure 3(b) shows the $T = 15$ K spectra of sample K-155 for both polarization directions. The strongly

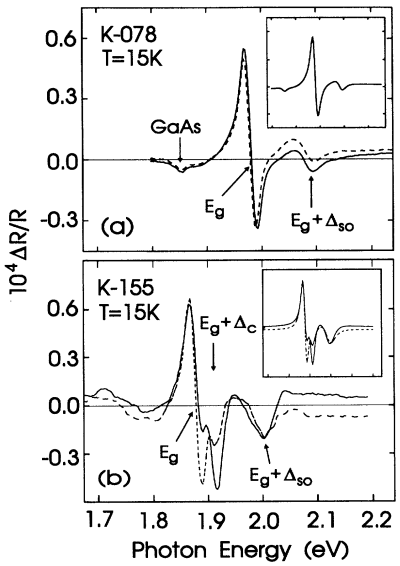

FIG. 3. Piezomodulated reflectivity spectra at 15 K with the polarization of the incident light along $[\bar{1}10]$ (continuous line) and [110] (dashed line). (a) Spectra for the highly disordered sample K-078. (b) Spectra for the partially ordered sample K-155. Note the strong ordering-induced Δ_c splitting in (b) that is absent in (a). The insets show line-shape fits obtained using a first derivative Aspnes functional form suitable for piezomodulated reflectivity.

TABLE I. Measured ($T = 15$ K) band gap E_g, and valence-band splittings Δ_c and Δ_{so} of OMVPE-grown $Ga_{0.5}In_{0.5}P/GaAs(001)$ epilayers. The substrate tilt θ, V/III ratio, growth rate (GR), and growth temperature T_g are also indicated. The transition energies were corrected for slight deviations from the lattice-matched composition at room temperature.

Sample	θ (deg)	V/III	GR (μm/h)	T_g (°C)	E_g (eV)	Δ_c (meV)	Δ_{so} (meV)
K-078	2	50	4.4	750	1.989	2	103
K-063	2	50	4.4	730	1.968	8	103
K-128	2	59	4.4	715	1.951	12	105
K-092	2	50	4.4	700	1.939	18	107
K-075	2	50	4.4	670	1.931	20	105
K-044	2	50	4.4	630	1.959	15	105
K-175	2	50	4.4	600	1.978	5	103
K-201	6	340	1.9	730	1.966	7	105
K-190	6	340	1.9	670	1.882	27	119
K-189	6	340	1.9	650	1.875	29	113
K-155	6	340	1.9	625	1.884	31	121

polarization-dependent dominant features near 1.9 eV correspond to transitions with energy E_g between the top of the valence band and the bottom of the conduction band, and transitions with energy $E_g+\Delta_c$ between the top of the valence band and the crystal-field split band. The $[\bar{1}11]$ ordering direction projects along $[\bar{1}10]$ on the sample surface, and thus the $E\|[\bar{1}10]$ polarization yields a strong $E_g+\Delta_c$ transition, comparable to the E_g transition, as seen in Fig. 3(b) (continuous line). On the other hand, the $E\|[110]$ polarization yields a strong E_g transition and a weak $E_g+\Delta_c$ transition (dashed line); this is consistent with polarization selection rules,[6] which indicate that the intensity of the E_g signature is three times larger than that of the $E_g+\Delta_c$ signature for this polarization. The energy difference between these two signatures yields a crystal-field splitting of $\Delta_c=31$ meV. The crystal-field splitting is a clear indication of the existence of a significant degree of CuPt ordering. The smaller features at 2.0 and 1.86 eV correspond to transitions involving the spin-orbit split-off band of the $GaInP_2$ epilayer and that of the GaAs substrate, respectively. Another effect of ordering is the lowering of the energy gap. At 15 K, the E_g of sample K-155 is 105 meV lower than that of the disordered sample mentioned above (K-078, see Table I), despite the fact that both samples have the same composition.

When the signatures are close in energy, as the E_g and $E_g+\Delta_c$ transitions, the line-shape fitting leads to difficulties in a unique determination of the splitting energy. We can resolve this ambiguity by using polarization selection rules[6] to determine the relative intensity of the two signals for both polarizations. These intensity relations have been used in the fitting procedure to obtain a better estimate of Δ_c; this is especially helpful for samples where the signatures are not clearly separated due to a small-crystal-field splitting. Table I gives the measured values for E_g, Δ_c, and Δ_{so}.

The general understanding of the microstructure of partially ordered $GaInP_2$, partly based on interpretations of electron microscope images, assumed the existence of ordered domains embedded in a disordered matrix. However, optical experiments do not yield signatures from the disordered matrix. Recent PL and PLE studies[8,9] have shown that partially ordered alloys consist of a statistical distribution of domains that exhibits different degrees of order, as seen in Fig. 4. Thus, in optical experiments sensitive to the various electronic transitions, such as piezomodulated reflectivity, no signatures from a disordered matrix are expected, but only signatures corresponding to an average degree of ordering close to the peak of the distribution η_p.

In addition, PZR and PLE techniques sensitive to upward absorptionlike transitions yield transition energies corresponding to the prevalent ordered domains in the volume of the epilayer. On the other hand, PL, a recombination process (after thermalizing and transport processes have taken place), depends on temperature through the Boltzmann occupation factor and yields transitions from lower energy levels corresponding to more ordered regions existing in the epilayer. We note that the Δ_c results of Kanata *et al.*[12] were measured in emission; hence, unlike our reflectance results, they depend on temperature through the Boltzmann occupation factor and thus probe the low-energy tail of the distribution of domains.

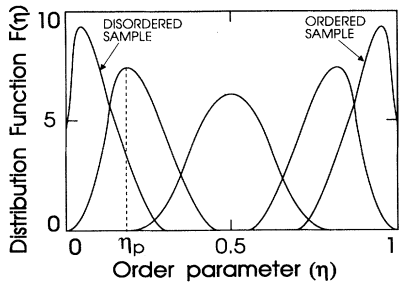

FIG. 4. Distribution function of partially ordered domains for various hypothetical samples exhibiting different degrees of ordering.

Figure 5 shows the E_g and $E_g+\Delta_c$ transitions at 15 K as a function of sample growth temperature for substrate misorientation $\theta=2°$ (continuous lines) and $\theta=6°$ (dashed lines). For a given misorientation, the bottom of the U-shape curve indicates the growth temperature (~670 °C) that yields the maximum degree of ordering (i.e., minimum E_g); this growth temperature also gives the maximum crystal-field splitting. It is also observed that a substrate misorientation of 6° enhances the degree of order relative to a 2° misorientation.

Figure 6 shows the valence-band splittings Δ_c and Δ_{so} as a function of band gap for $GaInP_2$ epilayers exhibiting different degrees of ordering. As expected, the crystal-field splitting increases as the band gap decreases (i.e., as

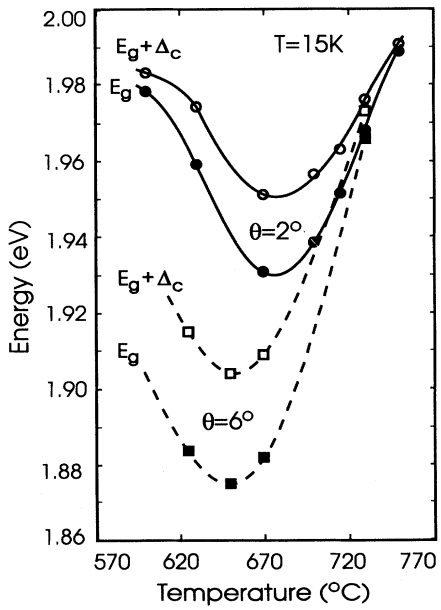

FIG. 5 E_g and $E_g+\Delta_c$ transitions at 15 K as a function of sample growth temperature for substrate misorientation $\theta=2°$ toward $[0\bar{1}1]$ (continuous lines) and $\theta=6°$ toward $\langle 111\rangle_B$ (dashed lines).

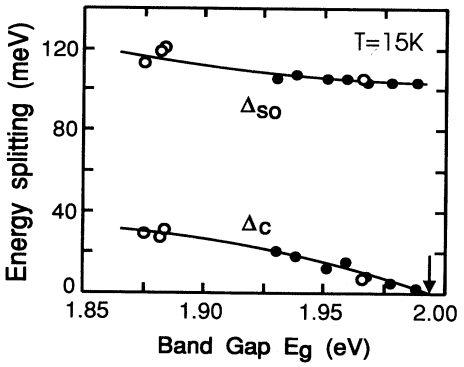

FIG. 6. Crystal-field splitting Δ_c and spin-orbit splitting Δ_{so} versus energy gap E_g for $GaInP_2$ epilayers exhibiting different degrees of ordering. Both substrate misorientations are considered: $\theta=2°$ toward $[0\bar{1}1]$ (solid circles) and $\theta=6°$ toward $\langle 111\rangle_B$ (open circles).

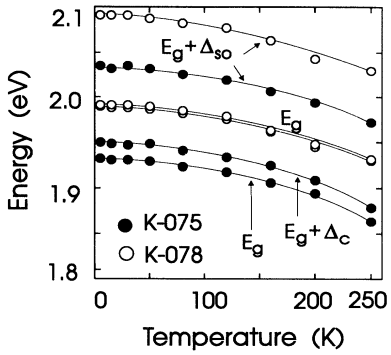

FIG. 7. Temperature dependence of the E_g, $E_g+\Delta_c$, and Δ_{so} transitions in ordered (solid circles) and disordered (open circles) $GaInP_2$.

ordering increases) as a result of an increasing departure from the zinc-blende symmetry. The spin-orbit splitting also shows an increase with ordering, as predicted by a theoretical model.[1] The valence-band splittings for both substrate misorientations, $\theta=2°$ (solid circles) and $\theta=6°$ (open circles), seem to exhibit a similar dependence on the band gap. The point of extrapolation $\Delta_c(E_g)\rightarrow 0$ (see arrow in Fig. 6) represents a perfectly disordered sample. The band gap of the projected random alloy lies 3 meV above that of K-078 (1.992 eV), our most disordered sample. An extrapolation of E_g vs temperature (see Fig. 7 below) for K-078 yields $E_g\sim 1.90$ eV at 300 K; this implies that $E_g(300\text{ K})\sim 1.903$ eV for the random alloy. Although there is no full agreement on what the band gap of perfectly disordered $GaInP_2$ is, liquid phase epitaxy (LPE) grown $GaInP_2$ is thought to yield the most disordered material with $E_g\sim 1.91$ at room temperature,[17] a value reasonably close to our estimate.

Currently, direct experimental measurements of the degree of ordering η are limited.[18,19] Theoretical relationships between η and the transition energies E_g, Δ_c, and Δ_{so} have been calculated for ordering in III-V alloys.[1] The predicted band-gap lowering of ~ 310 meV for perfect CuPt order in $GaInP_2$ indicates only a limited amount of ordering in the samples studied: fitting the measured ΔE_g and Δ_c to the theoretical model showed[20] $\lesssim 60\%$ ordering in the most ordered samples. Nuclear magnetic resonance (NMR) studies also indicate that OMVPE-grown samples that exhibit a band-gap lowering of ~ 100 meV yield a maximum amount of ordering of $\lesssim 60\%$.[19] Other theoretical work[21] estimated the maximum band-gap lowering for perfectly ordered $GaInP_2$ at ~ 100 meV, which would yield essentially 100% ordering for our most ordered sample. This appears to be inconsistent with the NMR experiment[19] and with transmission electron diffraction estimates.[18]

The temperature dependence of the E_g, $E_g+\Delta_c$, and $E_g+\Delta_{so}$ transitions is shown in Fig. 7. The figure shows the PZR results for an ordered (solid circles) and a predominantly disordered (open circles) $GaInP_2$ epilayer in the range from 6 to 250 K. As expected in semiconductors, E_g increases as the temperature decreases, with a region at low temperature where E_g is almost constant. Note the band-gap lowering and the crystal-field splitting in the ordered epilayer. Also note that the curves are parallel, indicating that the crystal-field splitting and the spin-orbit splitting do not depend on temperature, within experimental error. The line shapes of the PZR spectra do not change significantly as a function of temperature; this is in sharp contrast to PL measurements, where the low-temperature spectra favor the lowest energy transition and emission from the more ordered domains.

The strain-induced corrections to the valence-band splittings can be assessed by measuring them versus temperature in a highly disordered sample. Because ordering is minimal, the only source of splitting is strain. The latter can be modulated by changing the temperature because the thermal-expansion coefficients of the substrate and film are different. Thus, measuring Δ_c vs temperature provides a measure for strain-induced splitting. Because Δ_c was insensitive to temperature within experimental error, we estimate that the contribution of strain to the observed splittings is less than 2 meV.

To conclude, we have done a systematic PZR study of $GaInP_2$ epilayers grown by OMVPE on 2° and 6° misoriented [001] GaAs substrates. We have obtained experimental values for E_g, Δ_c, and Δ_{so} as a function of ordering and temperature. Our results are consistent with a statistical distribution of ordered domains and probe the peak of the distribution at temperatures ranging from 6 to 250 K.

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