Photoluminescence-excitation-spectroscopy studies in spontaneously ordered $GaInP_2$

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We present results of an experimental study of the optical properties of spontaneously ordered $GaInP_2$ using the techniques of low-temperature polarized photoluminescence and polarized photoluminescence excitation spectroscopy. Highly ordered samples are seen to have an absorption edge which is softer, more polarization dependent, and blueshifted farther from the PL peak than less-ordered samples. The data provide evidence for a statistical distribution of domains having different order parameters in epitaxial films of $GaInP_2$.

The band structure of spontaneously ordered GaInP₂ has been the subject of many recent studies.¹⁻³ Roomtemperature polarized photoluminescence (PL) experiments have shown¹ that violations of cubic symmetry selection rules occur due to the crystal-field splitting of the valence bands that is generated by the presence of long-range ordering in epitaxially grown films of this alloy. In this paper, we present results of our studies on the phenomenon of spontaneous ordering in GaInP₂ using the technique⁴ of photoluminescence excitation spectroscopy (PLE). In contrast to PL measurements, PLE measurements are sensitive to the joint density of states and thus yield information analogous to that obtained in absorption measurements. At low temperatures, our polarized PLE measurements on samples of GaInP2 exhibiting the phenomenon of spontaneous ordering indicate that (i) the absorption edge, as measured in PLE, is blueshifted with respect to the PL peak position; (ii) there is a crystal-field splitting of the absorption edge with the polarization of incident light; and, (iii) there is a softening of the slope of the absorption edge. These phenomena are correlated with the band-gap lowering (and hence the order parameter η) caused by the CuPt-type spontaneous ordering of the alloy. The data provide evidence for a statistical distribution of domains having different order parameters η in epitaxial films of GaInP₂.

A series of Ga_{0.52}In_{0.48}P epilayers was grown using organometallic vapor-phase-epitaxy (OMVPE) techniques on (001) GaAs substrates using the substrate growth temperature T_G as a variable,⁵ ranging from 630 °C to 750 °C. The growth rate, V:III ratio, and phosphine partial pressure were held constant at 4.4 μ m/h, 50, and 233 Pa, respectively. X-ray double crystal rocking curve measurements indicate that the lattice mismatch between these films and their substrates is less than 0.3%. A band-gap lowering⁶ was observed in these samples as a function of the substrate growth temperature, with the maximum lowering of the band gap of 75 meV occurring for a growth temperature of 670 °C. Transmission electron diffraction measurements indicate the presence of spontaneous CuPt-type ordering in samples grown under similar conditions.

It has been shown theoretically² that the zone folding resulting from CuPt ordering leads to a lowering of the conduction band, and the reduced symmetry results in a

crystal-field splitting of the valence bands.¹ This bandgap lowering and crystal-field splitting have been observed experimentally¹ using room-temperature polarized PL measurements. Cross-sectional transmission electron microscopy (TEM) studies indicate that the epilayers of spontaneously ordered GaInP2 are composed of CuPttype domains in which the cations are ordered. For any such domain, it was pointed out in Ref. 1 that partial ordering (order parameter $0 < \eta < 1$) leads to a superlattice composed of alternating Ga-rich $(Ga_{0.5+x}In_{0.5-x}P)$ and In-rich $(Ga_{0.5-x}In_{0.5+x}P)$ monolayers (in this case $\eta = 2x$). For perfect ordering $\eta = 1$, and the superlattice is comprised of pure GaP and InP monolayers. For both these situations, the structural transformation results in the symmetry changing abruptly from $F\overline{4}3m$ to the subgroup R3m, and the ordered structure belongs to a small set of Landau-Lifshitz ordered phases that can be derived from the parent zinc-blende alloy.² Although, for an equilibrium phase, the order parameter η should have a unique value (aside from normal statistical fluctuations) for a given growth temperature T_G , it is important to note that the CuPt phase is not the equilibrium phase in the bulk at any temperature. The local order parameter is a complex function of surface ⁷ and bulk chemical potentials and adatom and bulk interdiffusion. Thus, it is likely that these nonequilibrium processes will yield domains characterized by a distribution $F(\eta)$ of order parameters η in the range $0 \le \eta \le 1$ where

$$\int_{0}^{1} F(\eta) d\eta = 1 \quad . \tag{1}$$

The characteristics of this distribution $F(\eta)$ will depend on parameters such as substrate growth temperature, III/V partial pressure, and growth rate. Typically, the volumes probed in PL measurements have dimensions larger than a few hundred micrometers, whereas the typical size of domains observed in TEM measurements is < 1000 Å. PL intensities, which are sensitive to the product of the joint density of states and the Fermi probability distributions for electrons and holes, are dominated by contributions from small-band-gap domains with values of η above η_p , where η_p corresponds to the value where $F(\eta)$ has its maximum. This is because the Fermi distribution factor shows a selective preference for domains with lower band gaps, and this preference is

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even more exaggerated at low temperatures. In contrast, PLE measurements are sensitive to the "distribution" of the joint density of states $J(E,\eta)$ corresponding to the distribution $F(\eta)$ of domains in the volume being probed, so the dominant contribution to the PLE signal will come from domains having $\eta = \eta_p$. Thus, at low temperatures, one expects a blueshift of the PLE with respect to the PL that increases with the order parameter η . This is clearly seen in Figs. 1(a) and 1(b), which contrast the polarized PL and polarized PLE signals from a sample that exhibits a high degree of ordering with those from a sample which exhibits a low degree of ordering.

In order to determine the form of the absorption coefficient in an epitaxial film exhibiting spontaneous ordering, we have shown,¹ in Figs. 2(a) and 2(b), the symmetry of the conduction and valence bands at the Γ point of the Brillouin zone in zinc-blende and CuPt-type material. In spontaneously ordered GaInP₂, the experimentally observed⁸ crystal-field splittings are less than 20 meV, so the absorption edge will be influenced by transitions to the conduction band from the top of the valence band as well as from the crystal-field split-off band. Consider a domain with order parameter η , band gap E_g , and crystal-field splitting Δ_c . Let $\alpha_i^{(1)}(E,\eta)$ and $\alpha_i^{(2)}(E,\eta)$ denote its absorption coefficients at energy E, for the E_g and $E_g + \Delta_c$ transitions, respectively, for polarization along the direction $i = \langle Imn \rangle$ referred to the crystal-graphic axes of the substrate. The absorption coefficient



FIG. 1. PL (thin line) and PLE (thick line) spectra for (a) a more ordered sample ($T_G = 670$ °C) and (b) a less-ordered sampled ($T_G = 750$ °C). The PL emission spectra were analyzed with a linear polarizer P oriented along the indicated crystallographic direction. The PLE spectra were collected without an emission polarizer, but the polarization of the incident laser E vector, E_L , was fixed in the [110] and [110] directions (solid and dashed lines, respectively). The peak in (b) at 1.93 eV is a secondary PL feature.



FIG. 2. Γ -point symmetries of the conduction and valence bands for (a) disordered and (b) ordered Ga_{0.52}In_{0.48}P.

 $\alpha_i(E)$ in CuPt-type ordered material will be a superposition of the contributions from the E_g and $E_g + \Delta_c$ transitions for all domains in the volume being probed. Since E_g and Δ_c are monotonic functions of η , we can define integrated absorption coefficients $\alpha_i^{(1)}(E)$ and $\alpha_i^{(2)}(E)$, for the E_g and $E_g + \Delta_c$ transitions, respectively, to account for the contributions to $\alpha_i(E)$ from the various domains in the volume being probed.

$$\alpha_i^{(1)}(E) = \int_0^1 F(\eta) \alpha_i^{(1)}(E,\eta) d\eta , \qquad (2a)$$

$$\alpha_i^{(2)}(E) = \int_0^1 F(\eta) \alpha_i^{(2)}(E,\eta) d\eta .$$
 (2b)

If ordering is assumed to occur along [111], then this can be chosen¹ as the symmetry axis z' of the rhombohedral group 3m, with the [110] direction as the y' axis. $\alpha_i^{(1)}(E,\eta)$ and $\alpha_i^{(2)}(E,\eta)$ can be projected along the primed set of axes $\mathbf{x}', \mathbf{y}', \mathbf{z}'$, and the selection rules developed in Ref. 1 for the selection rules for transitions from Γ_4^v , Γ_5^v , and $\Gamma_6^v(2)$ valence-band states of the Γ_6^c conduction-band state can be used to determine the ratio of the absorption coefficients $\alpha_i(E)$ for polarization along the [110] and [110] directions referred to the crystallographic axes of the substrate.

$$\frac{\alpha_{[110]}(E)}{\alpha_{[1\bar{1}0]}(E)} = \frac{\alpha_y^{(1)}(E) + \alpha_{y'}^{(2)}(E)}{\frac{1}{3}\alpha_{z'}^{(2)}(E) + \frac{1}{3}[\alpha_{x'}^{(1)}(E) + \alpha_{x'}^{(2)}(E)]} .$$
 (3)

The momentum matrix elements that appear in the absorption coefficients in Eq. (3) have the following relationships:¹

$$\langle \Gamma_6^{v}(2)|p_{x'}|\Gamma_6^c\rangle = \langle \Gamma_6^{v}(2)|p_{y'}|\Gamma_6^c\rangle = \langle \Gamma_6^{v}(2)|p_{z'}|\Gamma_6^c\rangle ,$$

and

$$\langle \Gamma_{4,5}^{\nu}(2)|p_{y'}|\Gamma_6^c \rangle = \langle \Gamma_{4,5}^{\nu}(2)|p_{x'}|\Gamma_6^c \rangle = 3 \langle \Gamma_6^{\nu}(2)|p_{x'}|\Gamma_6^c \rangle .$$

Thus, it can be shown from Eq. (3) that

 $\alpha_{[110]}(E) > \alpha_{[1\overline{10}]}(E)$, for samples that show spontaneous CuPt-type ordering. A splitting of the absorption edge in polarized PLE measurements on spontaneously ordered GaInP₂ is therefore to be expected. This is clearly verified experimentally in Fig. 1(a), in which the more-ordered sample shows a half-maximum splitting of 15 meV, whereas the sample with minimal ordering in Fig. 1(b) shows a splitting of <1 meV. The PLE spectra of Fig. 1(b) show distinct n = 1 and 2 excitonic features in both incident laser polarizations. These features occur at 1.9833 and 1.9918 eV. Fitting these energy values to a simple hydrogenic model⁹ yields an excitonic binding energy of 11.3 meV for disordered Ga_{0.52}In_{0.48}P.

In the limiting case of a sample composed only of domains having perfectly disordered cations, the distribution function $F(\eta)$ can be expressed mathematically as a δ function centered at $\eta=0$. The absorption coefficient $\alpha_i(E)$ becomes equal to $\alpha_i^{(1)}(E,0)$ and shows a steep rising edge, as shown in Fig. 1(b), which describes a sample with a minimal amount of ordering. As the peak in the distribution function moves away from $\eta_p=0$ for the case of a sample showing no ordering, to $\eta_p > 0$, for a sample exhibiting spontaneous ordering, the integrated absorption coefficients $\alpha_i^{(1)}(E)$ and $\alpha_i^{(2)}(E)$ get smeared due to the finite spread in the distribution function $F(\eta)$ and the resultant staggering of the $\alpha_i^{(1)}(E,\eta)$ and $\alpha_i^{(2)}(E,\eta)$, respectively, in Eqs. (2) and (3). This results in a more gentle rising edge for the absorption coefficient $\alpha_i(E)$, as shown in Fig. 1(a) for the sample exhibiting a greater degree of spontaneous ordering.

To conclude, we have performed a systematic study of the phenomenon of spontaneous order in GaInP₂ using the techniques of PL and PLE. At low temperature, our polarized PLE measurements reveal (i) a blueshift of the absorption edge, as measured in PLE with respect to the PL peak position; (ii) a crystal-field splitting of the absorption edge with polarization of the incident light; and, (iii) a softening of the slope of the absorption edge. In addition, these phenomena are correlated with the band-gap lowering (and hence the order parameter η) caused by the CuPt-type spontaneous ordering of the alloy. The data provide strong evidence for a statistical distribution of domains having different order parameters in OMVPEgrown epitaxial films of GaInP₂.

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