Polarized Band-Edge Photoluminescence and Ordering in $Ga_{0.52}In_{0.48}P$

A. Mascarenhas, Sarah Kurtz, A. Kibbler, and J. M. Olson
Solar Energy Research Institute, Golden, Colorado 80401
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We present the first experimental evidence for the spontaneous breaking of cubic symmetry in the band structure of films of $Ga_{0.52}In_{0.48}P$ grown by organometallic-vapor-phase epitaxy on (100) GaAs substrates. We show how this effect is related to the spontaneous ordering of the alloy, and its correlation with the anomalous lowering of the band gap observed in these films.

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Spontaneous long-range ordering into the CuAuI, CuPt, and chalcopyrite structures has recently been observed in several normally disordered isovalent III-V alloys $A_xB_{1-x}C$.[1] In the case of the alloy $GaInP_2$ grown by organometallic-vapor-phase epitaxy (OMVPE) on (001) GaAs substrates, electron-diffraction studies reveal ordering of the cations on the group-III sublattice along $[\bar{1}11]$ or $[1\bar{1}1]$, two of the four ⟨111⟩-type directions (see Fig. 1).[2-5] A mechanims for this spontaneous long-range ordering has been proposed.[6] This mechanims consists of the following: (1) the alignment of Ga and In atoms into a series of alternate [110]-direction Ga-atom lines within each (001) plane, which is caused by the anisotropic site occupation affinity for column-III atoms because of their large bond-length difference, and the asymmetry in the direction for the dangling bonds; (2) the in-phase alignment of two Ga lines belonging to adjacent (001)-ordered planes, which is caused by the selective settling of Ga atoms on the (111)B microfacets of [110] step arrays. Thus, although bulk $GaInP_2$ is metastable[7] with respect to phase separation, the long-range ordering observed during epitaxial growth is a result of surface thermodynamic effects rather than bulk thermodynamic effects.[8]

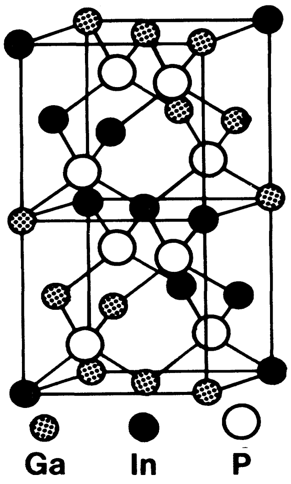

FIG. 1. Crystal structure showing the unit cell of the perfectly ordered alloy $GaInP_2$.

It has been observed that even at a fixed composition, the band gap of OMVPE-grown $GaInP_2$ varies with the reactor growth temperature, reaching a minimum at about 670 °C.[9-11] Excellent qualitative correlation between the degree of sublattice ordering and the lowering of the band gap in $GaInP_2$ has been reported.[2] However, there has been no conclusive evidence that the band-gap lowering is a result of spontaneous ordering. In the ordered alloy the size of the Brillouin zone is halved due to the doubling of the unit cell. As a result of this, the conduction-band state at the L point is zone folded back to the Γ point. This new state has the same symmetry as the conduction band at Γ[1] and lies just above it. The repulsion between these like-symmetry states results in a lowering of the band gap of the ordered alloy.[1] In addition, the reduced symmetry should result in a crystal-field splitting of the valence band, but this has not been previously observed.

In this Letter we present the first experimental evidence for the spontaneous breakdown of cubic symmetry in the band structure of spontaneously ordered films of $Ga_{0.52}In_{0.48}P$ grown by OMVPE on (001) GaAs substrates, misoriented 2° toward (011). Our results verify a direct correlation between the valence-band splitting, band-gap lowering, and ordering. For exciting light linearly polarized along the [110] or $[1\bar{1}0]$ crystal axis, we observe a shift in the energies of the room-temperature photoluminescence (PL) peaks for polarizations parallel (∥) and perpendicular (⊥) to that of the exciting light. The magnitude of this shift shows a correlation with the anomalous lowering of the energy gap of these films. The PL emission corresponding to each of these peaks shows a preference for polarization along the [110] or $[1\bar{1}0]$ crystal axis, respectively. The relative intensity of these two peaks for exciting light polarized along [110] differs from the relative intensity of the two peaks for exciting light polarized along $[1\bar{1}0]$. These results demonstrate an anisotropy between the [110] and $[1\bar{1}0]$ crystal axes, which are equivalent directions in the cubic-symmetry point group $\bar{4}3m$. The violations of cubic symmetry emerge as a natural consequence if the selection rules for optical transitions are derived for a band structure whose symmetry is that of the subgroup

$R3m$ instead of the full space group $F\bar{4}3m$. The results are consistent with those from structural measurements showing evidence of ordering in GaInP.[5,9-11]

Growth of $Ga_{0.52}In_{0.48}P$ films by OMVPE has been described earlier.[12] Samples 1 and 2 were grown at 700 and 750 °C, respectively. X-ray double-crystal rocking curves indicate that the lattice mismatch between the films and substrate is less than 0.1% and so the effects of strain on the bond structure can be neglected. Electron-diffraction studies reveal a higher degree of ordering in sample 1 as compared to sample 2. The PL was measured at room temperature using a perfect backscattering geometry.[13] A HeNe laser is used for the excitation. Exciting light is incident along the $\hat{z}$ direction, which is normal to the (001) face of the sample. PL emission in the $-\hat{z}$ direction is analyzed for polarization $\parallel$ and $\perp$ to that of the exciting light ($\mathbf{E}_i$). The energy gap of sample 1 is 1.83 eV, approximately 70 meV lower than the band gap of the fully random alloy $Ga_{0.52}In_{0.48}P$ grown by liquid-phase epitaxy.[2] The PL emission spectra for excitation polarized along (I) the [110] and (II) the [$1\bar{1}0$] crystal axes of this sample are shown by Fig. 2, curves *a* and *b*, 2(b), and by Fig. 2, curves *c* and *d*, respectively. The energy positions E_A and E_B of peaks *A* and *B*, respectively, remain unchanged for case I and case II. The energy difference $\Delta_{AB} = E_A - E_b = 10$ meV. The energy gap of sample 2 is 30 meV larger than that of sample 1. Figure 3 shows that the PL from sample 2 exhibits polarization features similar to those of sample 1. However, for this sample, $\Delta_{AB} = E_A - E_B = 2$ meV. To illustrate the polarization features of PL from a material which possesses the full cubic symmetry of $F\bar{4}3m$, we have performed similar measurements on the (001) face of a $Al_{0.28}Ga_{0.72}As$ sample. The PL spectra are shown in Fig. 4. Here, peaks *A* and *B* have the same energy. If $I_\perp$ is the intensity of PL polarized $\perp$ to $\mathbf{E}_i$, and $I_\parallel$ is the intensity of PL polarized $\parallel$ to $\mathbf{E}_i$, ${}^{110}R = {}^{110}(I_\perp/I_\parallel)_p$ is the ratio of the peaks of these intensities when $\mathbf{E}_i \parallel [110]$, and ${}^{1\bar{1}0}R = {}^{1\bar{1}0}(I_\perp/I_\parallel)_p$ is the corresponding ratio when $\mathbf{E}_i \parallel [1\bar{1}0]$. In $Al_{0.28}Ga_{0.72}As$, one observes that ${}^{1\bar{1}0}R = {}^{110}R > 1$. It has been shown that this linear polarization of the luminescence is due to the anisotropic momentum distribution of photocreated electrons.[14] Since the two ratios are equal, the PL shows no preference between equivalent directions in the point group $\bar{4}3m$, consistent with the cubic symmetry of

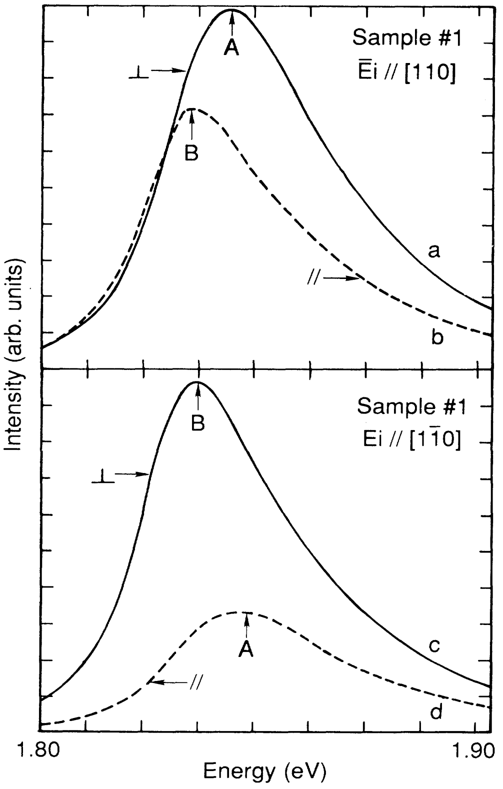

FIG. 2. For sample 1: PL emission polarized (curve *a*) $\perp$, (curve *b*) $\parallel$ for $\mathbf{E}_i \parallel [110]$ and (curve *c*) $\perp$, (curve *d*) $\parallel$ for $\mathbf{E}_i \parallel [1\bar{1}0]$.

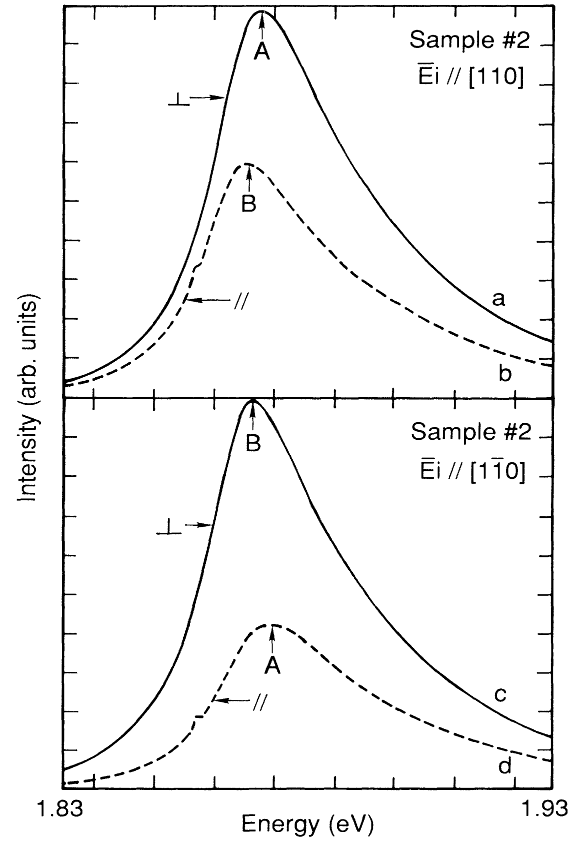

FIG. 3. For sample 2: PL emission polarized (curve *a*) $\perp$, (curve *b*) $\parallel$ for $\mathbf{E}_i \parallel [110]$ and (curve *c*) $\perp$, (curve *d*) $\parallel$ for $\mathbf{E}_i \parallel [1\bar{1}0]$.

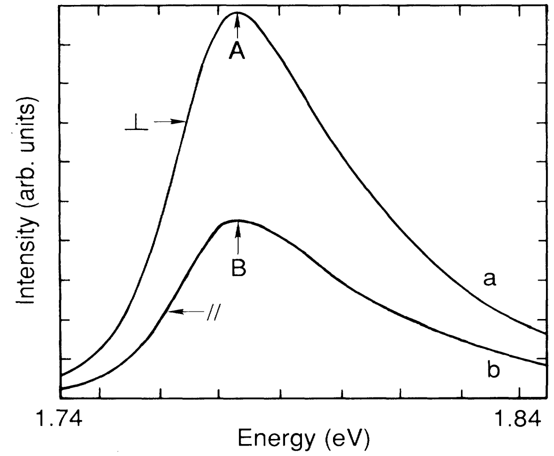

FIG. 4. For the $Al_{0.28}Ga_{0.72}As$ sample: PL emission polarized (curve *a*) ⊥ and (curve *b*) ∥ for $\mathbf{E}_i \parallel [110]$ or $[1\bar{1}0]$.

$Al_{0.28}Ga_{0.72}As$. However, for $Ga_{0.52}In_{0.48}P$, ${}^{1\bar{1}0}R > {}^{110}R > 1$, indicating a spontaneous breakdown of cubic symmetry.

We now consider the selection rules for optical transitions in $Ga_{0.52}In_{0.48}P$ using a band structure whose symmetry is that of the subgroup $R3m$ instead of the full space group $F\bar{4}3m$ and show that the above-mentioned discrepancies are a consequence of the reduced symmetry of this subgroup. We start by assuming that the cations are disordered on the group-III sublattice. For this situation, the symmetry of the band structure at the Γ point is described by the double group of $\bar{4}3m$ as shown in Fig. 5(a). Next, the cations are assumed to order on the group-III sublattice. Perfect ordering leads to a GaP/InP monolayer superlattice. Partial ordering leads to a superlattice comprised of alternating Ga-rich ($Ga_{0.52+x}In_{0.48-x}P$) and In-rich ($Ga_{0.52-x}In_{0.48+x}P$) monolayers. For both situations, however, the crystal symmetry changes abruptly from $F\bar{4}3m$. If the new symmetry is that of one of the subgroups of $F\bar{4}3m$, then the change can be described as a second-order phase transition.[15] Such a structural transformation is continuous. This makes it possible to treat the effects of ordering as a perturbation on the band structure of the disordered alloy. We assume the new symmetry to be described by the subgroup $R3m$. At the Γ point the evolution of the band structure in the environment of reduced symmetry is determined by the correlation of the point double groups of $3m$ and $\bar{4}3m$ as shown in Fig. 5(b). If ordering is assumed to occur along $[1\bar{1}1]$, then this is the direction of the symmetry axis $\hat{z}'$ of the rhombohedral group $3m$. The $[1\bar{1}1]$ and $[\bar{1}11]$ directions define a plane whose normal is along $[110]$. We choose this as the $\hat{y}'$ axis. The $[1\bar{1}0]$ and $[100]$ axes transform into the $[10\sqrt{2}]$ and $[0\bar{1}0]$ directions, respectively, in the primed coordinate system. The selection rules for optical transitions from the conduction band to the valence band (at Γ) and vice versa are derived by determining the nonvanishing momentum matrix elements between these states, for exciting light with polarization components along $\hat{\mathbf{x}}'$, $\hat{\mathbf{y}}'$, and $\hat{\mathbf{z}}'$. PL emission polarized along $\hat{\mathbf{x}}'$ and $\hat{\mathbf{y}}'$ is allowed for transitions from Γ_6^c to Γ_4^v, Γ_5^v, and $\Gamma_6^v(2)$. PL emission polarized along $\hat{\mathbf{z}}'$ is allowed only for transitions from Γ_6^c to $\Gamma_6^v(2)$. The transitions Γ_6^c to $\Gamma_6^v(1)$ have been ignored since at room temperature kT is much less than the spin-orbit splitting.

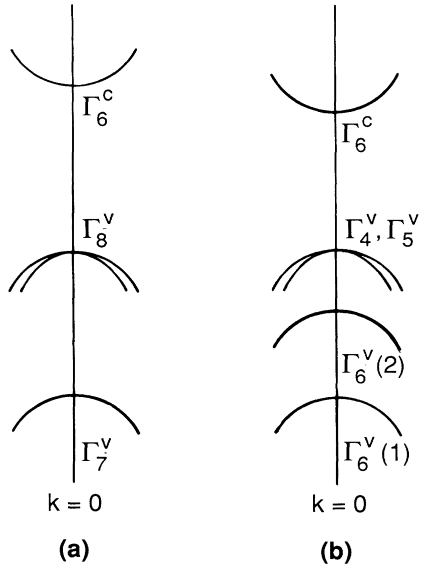

FIG. 5. Symmetry of the conduction and valence bands at the Γ point for (a) disordered and (b) ordered $Ga_{0.52}In_{0.48}P$.

If $(I_A)_\alpha$ is the intensity of PL emission with energy E_A and polarization along α (where $\alpha = x',y',z'$), and $(I_B)_\alpha$ is the intensity of PL emission with energy E_B and polarization along α (where $\alpha = x',y'$), then

$$ {}^{1\bar{1}0}\left[\frac{I_\perp}{I_\parallel}\right] = \frac{(I_B)_{y'} + (I_A)_{y'}}{\frac{2}{3}(I_A)_{z'} + \frac{1}{3}[(I_B)_{x'} + (I_A)_{x'}]}, \tag{1} $$

$$ {}^{110}\left[\frac{I_\perp}{I_\parallel}\right] = \frac{\frac{2}{3}(I_A)_{z'} + \frac{1}{3}[(I_B)_{x'} + (I_A)_{x'}]}{(I_B)_{y'} + (I_A)_{y'}}. \tag{2} $$

The superscripts and subscripts in Eqs. (1) and (2) are used to distinguish between the polarization of the exciting light and the PL emission, respectively. $\Delta_{AB} = E_A - E_B$ corresponds to the crystal-field splitting. Consider the PL emission polarized along $[1\bar{1}1]$. The matrix elements $\langle \Gamma_4^v | y' | \Gamma_6^c \rangle$, $\langle \Gamma_5^v | y' | \Gamma_6^c \rangle$, and $\langle \Gamma_6^v(2) | y' | \Gamma_6^c \rangle$ are each nonzero. The heavy- and light-hole valence subbands Γ_4^v and Γ_5^v comprise $J_{z'} = \pm\frac{3}{2}$ states ($J_{z'}$ is the z' component of the total angular momentum), whereas $\Gamma_6^v(2)$ comprises $J_{z'} = \pm\frac{1}{2}$ states. Also, Γ_4^v and Γ_5^v lie above $\Gamma_6^v(2)$ by energy Δ_{AB}. Hence, PL emission polarized along $[1\bar{1}0]$ results predominantly from the recombination between Γ_6^c and Γ_4^v,Γ_5^v, which yields the dominant peak B at energy E_B. Since the numerator and denominator of Eqs. (1) and (2) are reversed, PL emission polarized along [110] yields peak A as the dominant peak. The peak in the numerator of Eq. (1) is at energy E_B, whereas the peak in its denominator is at energy E_A. The reverse is true for Eq. (2). Since $E_B < E_A$, PL transitions with energy E_B are favored with respect to those with energy E_A. Thus, ${}^{1\bar{1}0}R > {}^{110}R$. Because of the anisotropic distribution of photocreated electrons, each of these ratios is greater than unity,[14] i.e., ${}^{1\bar{1}0}R > {}^{110}R > 1$.

To conclude, it is possible to explain the spontaneous breaking of cubic symmetry in the band structure of the $\mathrm{Ga_{0.52}In_{0.48}P}$ samples as a result of spontaneous ordering of this alloy along the $[1\bar{1}1]$ axis. Since ordering along the $[\bar{1}11]$ axis would have led to similar results, but ordering along [111] or $[11\bar{1}]$ would not, the results indicate that the samples are ordered predominantly along the $[1\bar{1}1]$ or $[\bar{1}11]$ axis, in agreement with electron-diffraction studies and the current understanding of the ordering mechanism. Our results verify a direct correlation between the valence-band splitting, band-gap lowering, and ordering.

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