Near-band-gap reflectance anisotropy in ordered Ga$_{0.5}$In$_{0.5}$P

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We present a theory that models the reflectance difference spectrum of bulk, spontaneously ordered Ga$_{0.5}$In$_{0.5}$P. Near the band gap $E_0$ this spectrum exhibits a sharp, negative feature at $E_0$ and a broad positive feature that peaks near $E_0 + \Delta_S$. The zero crossing between these two peaks occurs near $E_0 + \Delta_C$. For the sample studied in this paper, the spin-orbit splitting $\Delta_s$ and the crystal-field splitting $\Delta_C$ are 120 and 25 meV, respectively. Two previous calculations, which assume constant transition-matrix elements, were able to produce a negative peak at $E_0$, but not the positive feature. In this paper, the reflectance difference spectrum near the band gap is calculated using an 8-band $k\cdot p$ model and an explicit treatment of the momentum or $k$ dependence of the transition-matrix elements. The new calculation produces both the negative peak at $E_0$ and the positive feature that peaks near $E_0 + \Delta_S$. The positive feature is attributed to the strong $k$ dependence of the matrix element anisotropy. A strong coupling, enhanced by ordering, between three valence bands is essential. A problem associated with the analytical expression for the dielectric function $\varepsilon$ used in previous calculations is discussed. [S0163-1829(97)07224-X]

I. INTRODUCTION

Spontaneous ordering in III-V materials has been studied extensively in recent years. For Ga$_{0.5}$In$_{0.5}$P the most frequently observed form of ordering consists of alternating planes of Ga$_{0.5-y}In_{0.5-y}$P and Ga$_{0.5-y}In_{0.5+y}$P in the [111] direction where $\eta$ is the order parameter. This form of ordering is often referred to as CuPt-like. Associated with the ordering are two major electronic features: (1) the band gap $E_0$ is reduced,\(^5\) in some cases by more than 100 meV (Refs. 2 and 3) at the $\Gamma$ point, the valence-band maximum, fourfold degenerate in disordered Ga$_{0.5}$In$_{0.5}$P, is split\(^4\) with an energy difference $\Delta_C$. Theoretically, the ordering-induced shift of the band gap,\(^5\) $\Delta E_0$, and the valence-band splitting,\(^5\) $\Delta_C$, are to first order, quadratic functions of $\eta$. This implies that for samples with weak ordering ($\eta \approx 1$), detection of ordering in Ga$_{0.5}$In$_{0.5}$P by traditional optical techniques is difficult. This is consistent with previous experimental work using photoluminescence (PL),\(^4,7,8\) photoluminescence excitation (PLE),\(^7,10\) and modulated reflectance\(^11-14\) to measure $\Delta E_0$ and $\Delta_C$. Recently, however, reflectance difference spectroscopy (RDS) has been shown to be a more sensitive technique for detecting the presence of ordering in III-V alloys and can easily be adapted to in situ measurements during and after growth.\(^15-17\)

II. BACKGROUND

RDS measures the anisotropy of optical reflectance. In this study we let

$$\frac{\Delta R}{R} = \frac{(R_{1\bar{1}0} - R_{110})}{(R_{1\bar{1}0} + R_{110})/2},$$

where $R_{1\bar{1}0}$ and $R_{110}$ are the reflectances along [110] and [110], respectively. Originally, RDS was used to study the anisotropic surface reconstruction of III-V materials with isotropic bulk properties.\(^18\) The RD spectrum of an ordered III-V alloy generally exhibits both surface- and bulk-induced spectral features and, at times, it is difficult to separate the two effects.\(^15,16\) Recently, however, we have developed a technique for effectively quenching the surface-induced features in ordered Ga$_{0.5}$In$_{0.5}$P.\(^19\) (In short, this is accomplished by annealing the Ga$_{0.5}$In$_{0.5}$P in H$_2$ at a temperature of about 400 °C to achieve a group-III terminated surface and then exposing this surface to N$_2$ or air at room temperature.)

A typical bulk RD spectrum of (partially) ordered Ga$_{0.5}$In$_{0.5}$P is shown in Fig. 1. The important ordering-related RDS features are (1) a sharp, negative feature at $E_0$, (2) a broad, positive feature that peaks at $E_0 + \Delta_S$, and (3) a zero crossing between the two peaks that occurs near $E_0 + \Delta_C$. The sample of Fig. 1 was grown by metalorganic chemical vapor deposition using PH$_3$, trimethylgallium, and trimethylindium in a H$_2$ carrier gas. The input P to (In+Ga) ratio during growth was 60, and the growth temperature and rate were 670 °C and 5.5 μm/h, respectively. The layer was grown on a (001) GaAs substrate misoriented 6° toward (111)B. Details of the growth setup are described elsewhere.\(^15\) The sample was specularly smooth and closely lattice matched ($\Delta a/a < 10^{-3}$) to the underlying GaAs substrate. It contained a single CuPt-like ordering variant and the background doping density was below 10$^{16}$ cm$^{-2}$, n-type. These properties avoid complications introduced by strain effects,\(^20\) electro-optic effects\(^21\) associated with heavy doping, and anisotropic surface roughness effects associated with two-variant ordered Ga$_{0.5}$In$_{0.5}$P.\(^15,22,23\)

The observed optical anisotropy near $E_0$ has been investigated theoretically using 4-band\(^15,16\) and 6-band\(^24\) Luttinger models, where ordering related terms were added to the Hamiltonian by treating the effect of ordering in the same way that one would treat the effect of uniaxial strain. Both strain and/or ordering reduce the crystal symmetry and split the valence-band maximum. The 4- and 6-band models yield expressions for $\Delta R/R$ in terms of the band energies $E_i$ (i.e., $E_0$, $E_0 + \Delta_C$, and $E_0 + \Delta_S$) that characterize the effects of ordering in the material. These expressions are of the form...
where $c_0$ is a constant and $a_i = M_{i,(110)}^2 - M_{i,(110)}^2$ is the 
momentum matrix element anisotropy for the $i$th transition at 
energy $E_i$. (In this paper, we use the convention that the 
$\sqrt{x} = 0$ if $x < 0$.) For the 6-band model $a_0 = -(a_1 + a_2)$ and 
$a_1$ and $a_2$ are functions of $\eta$. For the 4-band model, it was 
assumed that $\eta \approx 1$, and, as a consequence, $a_2 \approx 0$ and 
$a_0 = -a_1$. The line shapes predicted by Eq. (2) (solid line) 
for the 4- and 6-band models are plotted in Figs. 2(a) and 
2(b), respectively. The 4-band model\cite{15,16} neglects the 
ordering-induced coupling between the crystal-field and the 
spin-orbit slit-off bands while the 6-band model\cite{24} includes 
this coupling in the calculation of the matrix elements and 
energy levels. Although both models produce a negative 
peak at $E_0$, neither is a good fit to the experimental line 
shape and neither reproduces the positive feature at $E_0 + \Delta_S$. One problem with both models is that the functional 
form of Eq. (2) (related to the form of $e_i$) is only accurate 
for photon energies near the critical point and for weakly 
ordered alloys. The more accurate function form (see the 
Appendix) is

$$
\frac{\Delta R}{R} = -\frac{c_0}{E^2} \sum_i a_i \sqrt{E_i - E - \sqrt{E_i - E}},
$$

(3)

shown as thin lines in Figs. 2(a) and 2(b). The fits, using Eq. 
(3), are somewhat better for photon energies less than $E_0$ but 
are still lacking for energies greater than $E_0$. We show in the 
following that the problem with both models [and with Eq. 
(3)] is the assumption that the matrix element anisotropy $a_i = 
M_{i,(110)}^2 - M_{i,(110)}^2$ is independent of $k$.

**III. THEORY**

In this paper, a new RDS calculation using an eight-band 
$k \cdot p$ model is presented. The $k$ dependence of the transition 
matrix elements is treated explicitly. This idea was stimu-
lated by the work of O’Reilly and Meney.\cite{25} They calculated 
the valence subband dispersion in strained quantum wells of 
ordered Ga$_{0.3}$In$_{0.7}$P and showed that the optical transition

![FIG. 1. Experimental RD spectrum of ordered Ga$_{0.3}$In$_{0.7}$P. The 
theory developed in this paper is only valid for photon energies in 
the vicinity of $E_0$ and $E_0 + \Delta_S$.](image1)

![FIG. 2. RD spectrum (open circle) and model calculations (thick 
lines): (a) 4-band model (Ref. 15), (b) 6-band model (Ref. 24), and 
(c) 8-band $k \cdot p$ model (this study). By varying $c_0$, the intensities 
of the RDS line shapes in (a), (b), and (c) are adjusted to fit the 
experimental intensity at $E_0$. The dashed line going through the data 
points is a guide to the eye. Although the resolution at $E_0$ is $\pm 25$ 
meV, spectra measured with higher resolution produce essentially 
the same line shape as that represented by the dashed line. The thin 
solid lines in (a) and (b) are line shapes calculated using the correct 
$k$ line shape for the 4- and 6-band models. Matrix elements are strongly anisotropic over a large region of 
k space. They also found that ordering plays a significant 
role in the coupling between the three valence subbands. More recently, Zhang and Mascarenhas\cite{26} have shown that 
the $k$ dependence of the matrix elements significantly affects 
the polarization of the excitonic states in ordered III-V al-
loys. Consequently, the usual assumption that the transition 
matrix element anisotropy is independent of $k$ is suspect. A 
treatment of the RDS problem using the $k$ dependence of 
matrix element anisotropy and the correct functional form 
for $e_i$ is discussed below. We show that this model is a 
much better fit to the RD spectrum of ordered Ga$_{0.3}$In$_{0.7}$P 
around $E_0$. More importantly, we show that the effect of the

![Image 2](image2)
order-induced coupling between the three valence bands at \( k \neq 0 \) cannot be neglected.

From the standard Fresnel equation for normal incidence reflectance, \( R = \left| \frac{\sqrt{e-1}}{\sqrt{e+1}} \right|^2 \), we first express Eq. (1) in a more general form,

\[
\Delta R / R = f(e_1, e_2) \Delta e_1 + g(e_1, e_2) \Delta e_2,
\]

where the dielectric function \( \varepsilon = (e^{110} + e^{110})/2 = e_1 + ie_2 \), and \( \Delta e_j = (e_j^{110} - e_j^{110}) \), \( j = 1 \) or 2. [Only linear terms in \( \Delta e_1 \) and \( \Delta e_2 \) are retained in the differentiation leading to Eq. (4).] In order to include the \( k \) dependence of the matrix elements, we use the following integral expressions for \( \Delta e_1 \) and \( \Delta e_2 \):

\[
\Delta e_1 = \sum \left( \Delta e_1 \right)_i = \sum \frac{2}{\pi (E_0)^{3/2}} \int_0^{x_m} \frac{a_i(x) \sqrt{x}}{[(1+x)^2 - \zeta_i^2](1+x)} \, dx,
\]

\[
\Delta e_2 = \sum \left( \Delta e_2 \right)_i = \frac{2}{\pi (E_0)^{3/2}} \int_0^{x_m} \frac{a_i(x) \sqrt{x}}{[(1+x)^2 - \zeta_i^2](1+x)} \, dx
\]

\[
\sum \left[ a_i(\zeta_i - 1) \sqrt{\zeta_i - 1} - a_i(-\zeta_i - 1) \sqrt{-\zeta_i - 1} \right],
\]

Although the \( k \cdot p \) method for calculating \( E_i(k) \) and \( M_i^2 \) becomes less accurate for large values of \( k \), it is nevertheless reasonably accurate for calculating \( \Delta M_i^2 \). This is illustrated in Fig. 3, where, for photon energies far from the band edge, \( \Delta M_i^2 \) approaches zero, as expected, since the ordering mainly perturbs the band structure in an energy range comparable to the crystal-field splitting. Similarly, this model should be more accurate for calculating \( \Delta e_i \) than \( e_i \). It is worth mentioning that this approach reduces to the expected limits: at \( k = 0 \), the \( a_i \)'s are equal to those calculated in the 6-band model, and if we let \( a_i(x) = a_i(x = 0) \), Eq. (3) is obtained from Eqs. (4) and (5a). Also, if we replace \( \Delta M_i^2 \) with \( M_i^2 \) in Eqs. (5a) and (5b), we then obtain the correct one-electron expressions for \( e_1 \) and \( e_2 \), respectively.

IV. DISCUSSION

Several other important assumptions are made in this new calculation. (1) In principle, \( e \) is a tensor for uniaxial Ga\(_{1-x}\)In\(_x\)P. Here, the ordering effect has been treated as a perturbation of \( e_1 \). (2) We assume the functional forms of \( e_1 \) and \( e_2 \) are not sensitive to the ordering-induced coupling between the valence bands. This has been observed by Phillips et al.\(^{17}\) and this assumption is also made in the 4- and 6-band models. (3) Equations (5a) and (5b) are in the framework of the parabolic approximation and ignore any nonparabolicity\(^{26}\) in the valence bands at \( k \neq 0 \). (4) We have ignored the contributions of the higher conduction and valence bands, which may contribute to the RD intensity for \( E > E_0 + \Delta \). (5) We have also ignored the influence of excitonic effects on the line shape.\(^{30}\)

The line shape predicted by this work (solid line) is plotted along with the experimental spectrum in Fig. 2(c). Compared to the line shapes from the 4- and 6-band models [Figs. 2(a) and 2(b)], the line shape calculated in this paper not only fits better the data below \( E_0 \), but also reproduces a portion of the positive feature at \( E_0 + \Delta \). Figure 3 shows the negative peak at \( E_0 \) is mainly due to the anisotropy of the topmost or heavy-hole-like valence band. The contributions
from the other two bands are positive at \(E_0\). The positive RDS feature at \(E_0 + \Delta \delta\) is due mainly to the spin-orbit split-off band modulated by strong, ordering-induced coupling between the valence bands for \(\mathbf{k} \neq 0\). This also suggests that the cause of the poorer fit in the 6-band model relative to this model is due to (1) neglecting the off zone center \((\mathbf{k} \neq 0)\) coupling and (2) the use of an incorrect expression for the \(\epsilon_1\) line shape. It is worth mentioning that the contribution to the RDS intensity for all three models from \(\epsilon_2\) is negligible for \(E < E_0 + \Delta \delta\).

In a previous work, Luo et al.\(^{16,31}\) showed experimentally that the RD peak intensity at \(E_0\), \(\Delta R/R|_{E_0}\), varied linearly with \(\sqrt{\Delta E_0} \propto \eta^2\) is the ordering-induced band-gap shift. The 4-band model (in the limit of \(\eta \approx 1\)) yields this result explicitly. The 6-band model yields a superlinear relationship between \(\Delta R/R|_{E_0}\) and \(\sqrt{\Delta E_0}\) due to “intensity borrowing” between the three valence subbands. In this work, we have not calculated the \(\eta\) dependence of \(\Delta R/R|_{E_0}\) but simply wish to point out that both the 4-band and 6-band models are not likely to produce the correct functional dependence for \(\eta \approx 1\) because of the incorrect \(\epsilon_1\) line shape and the \(\mathbf{k}\) dependence of \(\Delta M^c_1\). If the correct line shape is used, the 6-band model, for a given \(\eta\), overestimates the RDS intensity at \(E_0\) compared to the current 8-band model. Furthermore, at least theoretically, the peak intensity is also affected by line broadening effects. This is shown in Fig. 4. Here, we simulate line broadening effects by using a more general and accurate expression for the dielectric function,\(^{32}\) which explicitly includes a line broadening parameter \(\Gamma_0\):

\[
(\epsilon)_{\gamma}(\omega) = \epsilon_0 + M_1^2 c_0 E_i^{-1.5} \chi_0^{-2} (2 - \sqrt{1 + \chi_0} - \sqrt{1 - \chi_0}),
\]  

where \(\chi_0 = (E + i \Gamma_0)/\epsilon_i\). Since the \(\Delta R/R\) line shape is dominated by the \(\Delta \epsilon_1\) term we only plot \(\Delta \epsilon_1\). Using a modified form of the 4-band model (with \(a_0 = -a_{CF}\))Fig. 4 shows that the intensity of \(\Delta \epsilon_1\) decreases by a factor of 2 by varying the broadening parameter from 0 to 10 meV. A value of 59 meV was used by Kato et al.\(^{32}\) for fitting ellipsometry data of Ga\(_{0.5}\)In\(_{0.5}\)P. (The importance of line broadening in the study of the optical properties of semiconductors has also been pointed out by Tanguy.\(^{30}\) This may be the cause for the relatively large amount of scatter in the data used to construct the plot of \(\Delta R/R|_{E_0}\) versus \(\sqrt{\Delta E_0}\) by Luo et al.\(^{16,31}\)

(We conjecture that the wide range of growth conditions required to yield a variety of samples with widely different band gaps also leads to samples with widely different broadening parameters.) Finally we would like to point out that although the theory presented in this paper does at least qualitatively reproduce both the negative peak at \(E_0\) and the positive peak at \(E_0 + \Delta \delta\), there is still a shoulder on the high-energy side of the latter that remains unexplained. It may be related to the folded \(\mathbf{k}\) band. Work is continuing in an effort to explain quantitatively the origin of this spectral feature.

V. CONCLUSION

In conclusion, we have presented a model using an 8-band \(\mathbf{k} \cdot \mathbf{p}\) theory that yields an RDS line shape near \(E_0\) comparable to that which is observed experimentally. The success of this models depends critically on the explicit treatment of the \(\mathbf{k}\) dependence of the transition-matrix elements. In particular, the strength and the line shape of the spin orbit feature are primarily determined by the ordering-induced \(\mathbf{k}\)-dependent anisotropy of the transition-matrix element. We have also pointed out that, to test an RDS model, a line-shape comparison to the experimental data is more meaningful than a single point measurement or calculation of intensity at some critical point. A discussion related to the incorrect functional form of \(\epsilon_1\) used in previous calculations is given in the Appendix.

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APPENDIX

As noted earlier, the functional form of \(\epsilon_1\) (and \(\Delta \epsilon_1\)) used in both the 4- and 6-band models is incorrect due to an incorrect Kramers-Kronig transformation. The fundamental physical requirements for both \(\epsilon_1\) and \(\epsilon_2\) are\(^{26,30}\)

\[
\epsilon_1(E) = \epsilon_1(-E) \quad \text{(even function),} \quad (A1)
\]

\[
\epsilon_2(E) = -\epsilon_2(-E) \quad \text{(odd function).} \quad (A2)
\]

The correct functional forms of \(\Delta \epsilon_1\) and \(\Delta \epsilon_2\) that satisfy Eqs. (A1) and (A2), and Kramers-Kronig (KK) relations can be obtained from Eqs. (5a) and (5b) by ignoring the \(\mathbf{k}\) dependence of \(a_1\):\(^{27,28}\)

\[
[\Delta \epsilon_2(E)]_i = \begin{cases} 
(a_i c_0 E_i^2) \sqrt{E - E_i}, & E \geq E_i, \\
0, & -E_i < E < E_i, \\ 
-(a_i c_0 E_i^2) \sqrt{-E - E_i}, & E < -E_i.
\end{cases}
\quad (A3)
\]
\[ \Delta \varepsilon_1 (E) = \varepsilon_0 + (a_i c_0 / E^2) (2 \sqrt{E_i - \sqrt{E} + \sqrt{E_i - E}}) \]

Only the \( E > 0 \) part of Eq. (A4) was used by the 4- and 6-band models. Although this omission violates the condition of Eq. (A2), it has no effect on the physical correctness of \( \Delta \varepsilon_2 \). However, it has a significant effect on the KK transformation of \( \Delta \varepsilon_2 \) to \( \Delta \varepsilon_1 \). Consequently, Eq. (2) (which is proportional to \( \Delta \varepsilon_1 \)) violates the requirement described in Eq. (A1).