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Band-gap reduction and valence-band splitting of ordered $GaInP_2$

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Low-temperature photoluminescence excitation spectra are used to determine the order-dependent parameters: valence-band splitting and band-gap reduction in spontaneously ordered $GaInP_2$. Effects due to composition fluctuations between different samples and the associated strain, as well as the excitonic binding energies, have been properly taken into account to yield accurate band-gap reduction and valence-band splitting values. The results from recently published *ab initio* band structure calculations are used to extrapolate the band-gap reduction from the strongest experimentally realized degree of ordering to perfect ordering. We find a total band-gap reduction of 471 ± 12 meV, which is very close to recent theoretical predictions. © *1995 American Institute of Physics.*

The phenomenon of spontaneous long-range ordering in several III–V zinc-blende semiconductors has been studied by a number of groups both experimentally and theoretically. In the case of $GaInP_2$, the ordered state is represented by the $CuPt_B$ structure. Growing the material by metalorganic vapor phase epitaxy (MOVPE) offers a wide range of growth conditions that result in different values of the order parameter η.[1] Crystal ordering strongly affects the electronic properties of $GaInP_2$. Order-dependent band-gap reduction (BGR) and valence-band splitting (VBS) have been predicted theoretically[2] and demonstrated experimentally.[3,4]

The first quantitative theoretical predictions of VBS and BGR for perfect ordering in $GaInP_2$ were published in 1989.[2,5] Nevertheless, there are very few experiments published that allow us to determine simultaneously the BGR *and* VBS of a series of samples with varying order parameter. This is mainly because the results of optical spectroscopy on ordered $GaInP_2$ samples show some unusual features, which are the subject of a series of papers.[6–10] (1) It has been[6] that low-temperature photoluminescence spectroscopy (PL) is not able to yield precise values for the band-gap energy because either the PL spectrum consists of several peaks that are not yet understood, or the PL peak moves with varying excitation density and shows an extremely large Stokes shift. (2) On the other hand, even photoluminescence excitation spectroscopy (PLE) was unable to yield a precise measure of the band gap of ordered samples, because no sharp excitonic maxima were detected. This latter phenomenon was attributed to an inhomogeneity in order parameter η within the samples.[11]

We present a study of the correlation between BGR and VBS based on low-temperature PLE spectra. The high quality of our samples results in clearly resolved excitonic maxima of both valence band edges and allows for a direct determination of the splitting in the valence band and the excitonic transition energy of a series of samples. These data are compared with recent band structure calculations by Wei, Mäder, and Zunger.[2,12–16]

We have grown a series of samples of bulk $GaInP_2$ by means of low-pressure MOVPE, as described in more detail in Ref. 10. The degree of ordering is influenced by varying the growth temperature between 660 and 840 °C, the substrate misorientation ($6°\rightarrow[111]_A$ and 6°, 10°, $15°\rightarrow[111]_B$), and the growth rate (0.5...2.0 μm/h). The V/III ratio was kept constant at 240. As can be seen in Table I, the order parameters cover the range from $\eta=0.0$ to $\eta\approx0.54$.

Figure 1 shows typical PLE spectra from an ordered sample. Two absorption maxima are clearly resolved. As described in the figure caption they show the expected dependence on the polarization of the incident light. The spectra, which are all taken at $T=2$ K, allow us to determine the parameters E_x and ΔE_{VBS} with an uncertainty of less than 1 meV, E_x being the $k=0$ transition energy of the free

TABLE I. Samples of bulk $GaInP_2$ used in this work. Substrate misorientation and growth temperature T_g have been varied to obtain different order parameters η. The measured (and corrected) values of E_x and ΔE_{VBS} are given in columns 5 and 6. η is calculated from ΔE_{VBS} using Eqs. (1) and (2).

Sample No.	Substrate	T_g (°C)	E_x (eV)	ΔE_{VBS} (meV)	η
1	$6°\rightarrow[111]_A$	840	2.007	0	0.0
2	$6°\rightarrow[111]_A$	810	2.009	0	0.0
3	$6°\rightarrow[111]_A$	750	1.988	3.5	0.23
4	$6°\rightarrow[111]_A$	720	1.976	6.9	0.23
5	$15°\rightarrow[111]_B$	690	1.973	7.6	0.24
6	$6°\rightarrow[111]_A$	690	1.973	10.0	0.28
7	$6°\rightarrow[111]_A$	660	1.973	11.0	0.30
8	$6°\rightarrow[111]_A$	660	1.971	11.8	0.31
9	$6°\rightarrow[111]_B$	750	1.957	11.3	0.30
10	$10°\rightarrow[111]_B$	690	1.916	21.0	0.43
11	$6°\rightarrow[111]_B$	720	1.914	21.7	0.44
12	$6°\rightarrow[111]_B$	690	1.893	26.5	0.49
13	$6°\rightarrow[111]_B$	660	1.886	26.8	0.50
14	$6°\rightarrow[111]_B$	690	1.885	27.7	0.51
15	$6°\rightarrow[111]_B$	660	1.879	29.5	0.54

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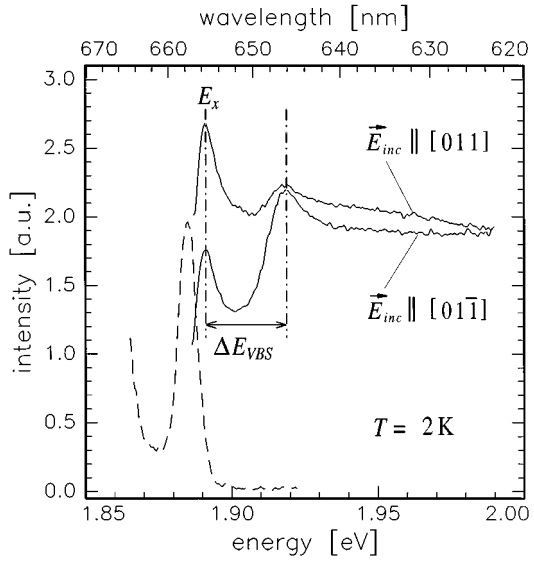

FIG. 1. Typical PLE spectra from an ordered sample (sample No. 12). The corresponding PL is plotted with dashed lines. The two PLE spectra are taken with different polarization of the exciting laser light with respect to the ordering planes. As predicted by theory, the optical transition with the upper valence band is stronger for optical polarization parallel to the ordering planes ($\mathbf{E}_{\mathrm{inc}} \| [011]$).

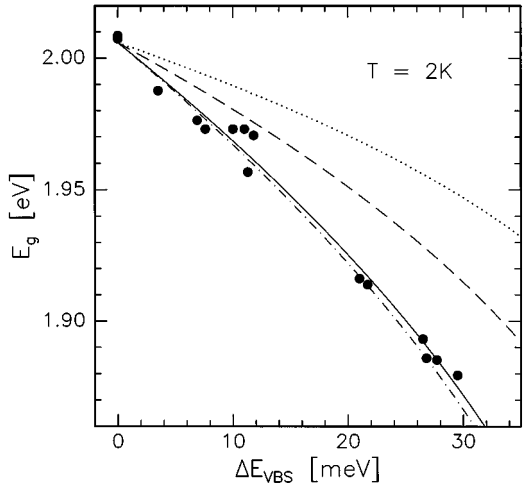

FIG. 2. Solid points: Values of E_g and ΔE_{VBS} of our samples. The excitonic transition energy is corrected for the crystal composition $Ga_{0.52}In_{0.48}P$. Dotted and dashed lines: Prediction by Wei and Zunger (Refs. 13 and 14), calculated with the parameters $E_g^{(0)}=2.005$ eV, $\Delta E_g^{(1)}=320$ meV, and $\Delta_{\mathrm{CF}}^{(1)}=200$ meV (dashed), and $\Delta_{\mathrm{CF}}^{(1)}=310$ meV (dotted). Dash-dotted line: Prediction by Mäder and Zunger (Refs. 15 and 16). Parameters: $E_g^{(0)}=2.005$ eV, $\Delta E_g^{(1)}=490$ meV, and $\Delta_{\mathrm{CF}}^{(1)}=200$ meV. Solid line: Best fit to our data, using the correlation between ΔE_G and ΔE_{VBS} by Wei and Zunger. Fitted values: $E_g^{(0)}=2.005$ eV, $\Delta E_g^{(1)}=471$ meV. Fitted with $\Delta E_{\mathrm{CF}}^{(1)}$ held constant at 200 meV.

(heavy-holelike) exciton (correlated with the upper valence-band, $\Gamma_{4,5}^V$), and ΔE_{VBS} being the energy separation between that latter exciton and the one that is formed with the lower valence-band $\Gamma_6^V(2)$ (light-holelike).

The measured values of E_x and ΔE_{VBS} can be influenced by compositional fluctuations from sample to sample due to (1) the band-gap dependence on composition, and (2) the influence of strain on the band edges. This uncertainty has been eliminated by measuring the lattice mismatch between each of the films and the GaAs substrate by means of high-resolution x-ray diffractometry (room temperature). In each case, the lattice mismatch was found to be below 10^{-3}. Using a theoretical correlation between lattice mismatch and band gap as calculated by Krijn,[17] we have determined the correction on E_x for a fictitious composition of $x_{\mathrm{Ga}}=0.520$. This is the composition used by most other authors. The strain effect on ΔE_{VBS} due to a deviation from the strain-free composition has also been corrected. This has been done by applying a perturbative calculation method as used in Ref. 14.

Table I and Fig. 2 contain values of E_x and ΔE_{VBS} *after* correction.

Moreover, the measured parameters E_x and E_{VBS} are possibly influenced by a variation of the excitonic binding energy E_B^{ex} with η, and a difference in E_B^{ex} for the two excitons formed with the upper and the lower valence bands. We have recently calculated the conduction band and valence band effective masses m^* in $GaInP_2$ as a function of the order parameter using an eight-band $k\cdot p$ model.[18] The effective masses are found to be anisotropic between the directions parallel and perpendicular to the ordering axes (i.e., $[111]$ or $[\bar{1}\bar{1}\bar{1}]$). Using the m^* obtained in Ref. 18, we applied a variational method[19] to calculate exciton binding energies for the heavy-holelike (hh) and the light-holelike (lh) bands. We find that (1) E_B^{ex} for both exciton states only varies by about 1 meV with η. The calculated values are: $E_B^{ex}(\eta=0)=6.2$ meV, $E_B^{ex}(\eta=1)=5.3$ meV. (2) The difference in E_B^{ex} between the two excitons is very small ($\sim$0.1 meV), because m^* along the ordering direction is heavier for the hh states and, on the other hand, in the plane perpendicular to the ordering direction, is heavier for the lh states, and the mass anisotropy is relatively small for the conduction band (which has lighter mass than the valence bands).

Both results (1) and (2) show that the measured parameters E_x and ΔE_{VBS} can be used as a valuable measure for the band-gap energy E_G and the valence-band splitting, respectively, without being corrected for exciton binding energy effects. We therefore set $E_x=E_g$ in the following.

Figure 2 shows a plot of the (composition corrected) values of E_g and ΔE_{VBS} of the samples listed in Table I. The dotted and dashed lines represent theoretical predictions by Wei, Mäder, and Zunger.[13–16] They are calculated using the following equations

$$\begin{aligned} &E_g(\eta)=E_g^{(\eta=0)}-\Delta E_g^{(\eta=1)}\cdot\eta^2, \\ &\Delta E_{\mathrm{VBS}}(\eta)=E_1(\eta)-E_2(\eta). \end{aligned} \tag{1}$$

The valence-band maxima E_1 and E_2 can be calculated as a function of η by means of the formulas given in Ref. 13.

$$\begin{aligned} &E_1=\tfrac{1}{2}(\Delta_0+\Delta_{\mathrm{CF}}), \\ &E_2=\tfrac{1}{2}[(\Delta_0+\Delta_{\mathrm{CF}})^2-\tfrac{8}{3}\Delta_0\Delta_{\mathrm{CF}}]^{1/2}, \end{aligned} \tag{2}$$

with the spin-orbit splitting and crystal-field splitting parameters Δ_0 and Δ_{CF}. These parameters also depend quadratically on η; values for $\eta=0$ and $\eta=1$ for both parameters are

given in Ref. 13. Elimination of η in Eqs. (1) leads to the correlation between E_g and ΔE_{VBS} which is used in Fig. 2.

As discussed in Ref. 13, the crystal-field splitting parameter $\Delta_{\mathrm{CF}}^{(\eta=1)}$ depends on whether the rhombohedral distortion along [111] of the ordered CuPt structure is relaxed (rhombohedral structure, $\Delta_{\mathrm{CF}}^{(1)}=310$ meV) or unrelaxed [cubic structure, coherent with the (100) GaAs substrate, $\Delta_{\mathrm{CF}}^{(1)}=200$ meV]. It can be seen in Fig. 2 that the dotted line, which is plotted for a relaxed structure, lies clearly above the data points. This suggests that the ordered material is realized as a cubic layer (unrelaxed), i.e., the epitaxial film is grown in coherence with the substrate. This is in good agreement with results from diffractometry. The other theoretical curves, as well as our fit, therefore assume $\Delta_{\mathrm{CF}}^{(1)}=200$ meV.

The calculations by Wei and Zunger lead to a maximum band-gap reduction of $\Delta E_G^{(1)}=320$ meV. More recent calculations by Mäder and Zunger, however, gave $\Delta_G^{(1)}=490$ meV. Curves corresponding to both values [represented by the dashed (Wei) and the dash-dotted (Mäder) lines] are compared with our data in Fig. 2. Because both theoretical values do not yield exact agreement with the experimental data, we have used the correlation $E_G=f(\Delta E_{\mathrm{VBS}})$, as given by Eqs. (1) and (2), to fit the parameter $\Delta E_G^{(1)}$. The best fit was achieved with $\Delta E_G^{(1)}=471\pm12$ meV, represented by the solid line in Fig. 2. Thus the ratio $\Delta E_G^{(1)}/\Delta_{\mathrm{CF}}^{(1)}$, which is independent of the exact value of $\Delta_{\mathrm{CF}}^{(1)}$, is found to be 2.36 ± 0.06. This result suggests that the more recent theoretical value of $\Delta E_G^{(1)}=490$ meV is closer to the experiment than the earlier value. Moreover, we point out that the value calculated by Kurimoto and Hamada[5] is definitely too low. These authors predicted a total band-gap reduction of 150 meV for perfectly ordered $GaInP_2$.

Previously, the theoretical prediction of BGR and VBS of ordered $GaInP_2$ has been compared[14] with experimental results by Alonso *et al.*[20] If we fit the function $E_G=f(\Delta E_{\mathrm{VBS}})$ used above to these data, we get a value of $\Delta E_G^{(1)}=406\pm28$ meV. It can be seen from the higher variance that these data are much more influenced by scattering than ours. Especially, the data points from stronger ordered samples scatter considerably, which makes the extrapolation to perfect ordering ($\eta=1$) very difficult. Moreover, Alonso *et al.* had to use a fitting procedure to evaluate the band-gap values from their reflectance spectra, a procedure that may introduce systematic errors. Note that our data are based directly on the measured PLE spectra, without any numerical treatment of the data (except from composition correction).

In summary, we have presented a study of the correlation between band-gap reduction ΔE_g and valence-band splitting ΔE_{VBS} in $GaInP_2$ due to $CuPt_B$ type of long-range ordering.

The very high homogeneity of both composition and degree of order throughout the samples allowed us to clearly resolve two excitonic maxima in the PLE spectra. These peaks are connected with the two valence-band maxima, and their separation gives a direct measure of the valence-band splitting energy ΔE_{VBS}.

A comparison of these data with theoretically calculated curves ΔE_g as a function of ΔE_{VBS} shows that the recently calculated band-gap reduction of 490 meV for perfect ordering is very close to our experimental value, which is extrapolated from $\eta<0.55$ to $\eta=1$ by means of the above-cited theory. This fitting procedure yields a value of $\Delta E_G^{(1)}=471\pm12$ meV, and $\Delta E_G^{(1)}/\Delta_{\mathrm{CF}}^{(1)}=2.36\pm0.06$.

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[1] The order parameter of $GaInP_2$ is defined by the composition of the alternating Ga- and In-rich monolayers: Ordered material consists of a sequence of layers ($Ga_{1+\eta}In_{1-\eta}P_2$) and ($Ga_{1-\eta}In_{1+\eta}P_2$) oriented perpendicularly to a [111]-direction.
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