Carrier Relaxation and Exciton Bleaching in Spontaneously Ordered GaInP

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Using time-resolved small-signal exciton absorption bleaching at low temperature, the optical transition energies from all three valence bands in spontaneously-ordered GaInP have been measured with high accuracy. The origin of the bleaching signal and the contributions of binding energy are discussed. With three measured energies from each sample, all parameters in the quasi-cubic perturbation model can be fitted. Good agreement is obtained with a spin−orbit splitting parameter of 103 meV, nearly independent of the degree of ordering. The ratio of bandgap reduction to crystal-field splitting parameter is found to be 2.7, slightly higher than in previous works. This difference is attributed to a more accurate determination of light-hole-like bandgap energy.

When GaInP is grown in the [001] direction under special conditions of temperature, growth rate and substrate misorientation, the cations deposit in alternating [111]-oriented Ga-rich and In-rich planes [1]. The band structure of the partially-ordered case has been studied by treating the ordering as a perturbation similar to the case of strain, deriving the order-dependence of the perturbation parameters, then matching the results to first-principle calculations of the completely ordered and disordered cases [2, 3]. Bandgap reduction, valence-band splitting (VBS), and a weak dependence of the spin−orbit splitting were predicted [3]. These have been observed [4, 5], however, an accurate, direct measurement of both VBS and spin−orbit splitting has not previously been possible.

In this paper we use careful substrate removal to prepare a set of free-standing samples with PL linewidths similar to [5]. This makes possible transmission measurements, which can access optical transitions high above the absorption edge. Their spectral resolution is greatly enhanced by using a nonlinear absorption-bleaching experiment. The optical transition energies of the heavy hole-like (HH), light hole-like (LH), and spin−orbit (SO) excitons are observed well resolved from their respective absorption bands.

Linear and differential absorption (DA) were measured with a 10 kHz ultrafast laser system. For the DA measurement, a 100 fs pump pulse at 2.2 eV excited the sample, creating an electron−hole population that quickly relaxed to the band minima. The quasi-equilibrium population modifies the absorption, which was measured by a fs white-light continuum pulse. The dotted curve in Fig. 1a shows the linear absorbance, αL, of a typical GaInP ordered sample at 5 K with the light polarization oriented parallel to the in-plane projection of the ordering axis. HH and LH peaks are only marginally resolved

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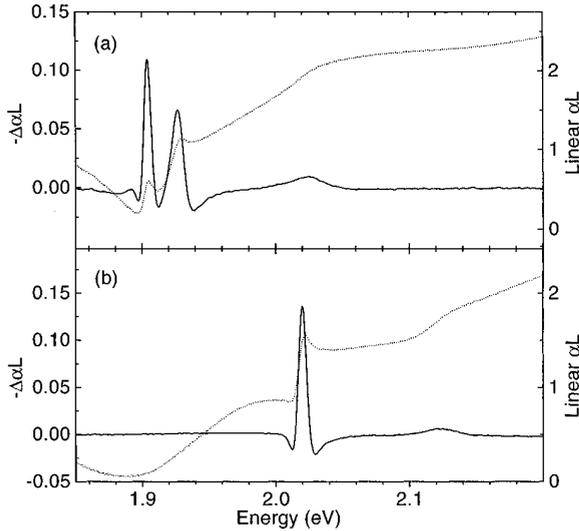
Fig. 1. Linear (dotted curve) and differential (solid curve) absorbance for a 5 K a) strongly ordered GaInP sample, and b) a nominally random alloy. The DA measurement used an excitation pulse of 100 fs, at 2.19 eV with a fluence of 10^{-6} J/cm^2 in a spot size of 250 μm giving an estimated carrier density of 3×10^{16} cm^{-3}. The pump–probe delay was 20 ps

from their absorption bands. Furthermore, very little precision is possible at the SO peak, where only a very broad shoulder is seen.

In the DA technique, one measures the *change* in linear absorption caused by an optically excited carrier density. As discussed below, using carefully chosen experimental parameters one can observe a signal at the exciton energies only, without contributions from the strong continuum absorption. This is plotted in the solid curve of Fig. 1a. For this to be an accurate locator of exciton absorption peaks, the signal must be attributed to a mechanism known to be spectrally coincident with the exciton to within the precision of these measurements (≈ 0.5 meV). We here argue that the signal is entirely excitonic, i.e., from screening of the Coulomb interaction responsible for exciton absorption, or from blocking of those states. Clearly the signal of Fig. 1 is sharply isolated at each band edge, with no obvious bleaching of continuum states. This is consistent with the experiment's long delay time and low excitation density. The density is well below that for exciton ionization, as evident from the small ratio of DA magnitude to linear absorption magnitude.

Furthermore, the earlier dynamics of the signal (not shown) contain only limited evidence for blocking of continuum or exciton states. Continuum blocking by the hot carriers should appear as an early, broadband, rapidly-cooling bleaching. Phase-space filling of the HH exciton can be recognized from a slow (ps) increase of the HH signal during the final stages of cooling. Both of these effects are seen with excitation densities higher than that used in Fig. 1. In contrast, for the excitation density of Fig. 1, there are no resolvable dynamics beyond a fast initial rise of the exciton peaks and a slow reduction in the induced absorption below the HH. From these considerations we assign the DA bleaching peaks in Fig. 1 primarily to screening, with a possible smaller contribution from phase-space filling. By using exciton bleaching, the energies can be precisely located even in samples where the linear absorption peaks are not well resolved from the continua, or in the case of the SO peak, not seen at all.

The variations of exciton binding energies between valence bands and with degree of ordering have been considered. Using the anisotropic effective masses calculated in Refs.
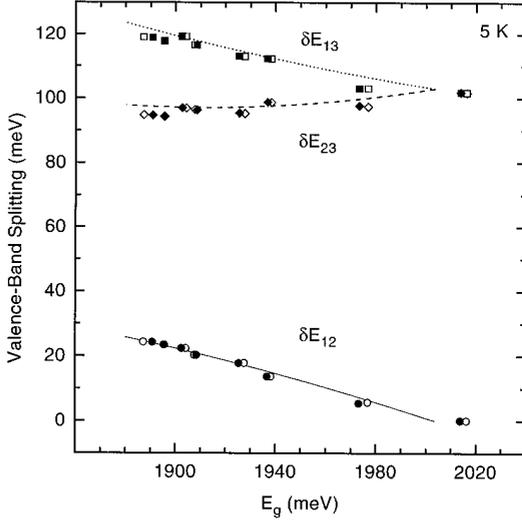
Fig. 2. Energy gap differences for 5 K GaInP plotted against the HH peak energy. Experimental conditions were identical to Fig. 1. Discrete points: Experimentally measured SO splitting (δE_{13}), VBS (δE_{12}), and their difference (δE_{23}). Open points are original data, solid points are data corrected for lattice and composition mismatch through X-ray measurements. The precision of the DA measurement at a fixed sample location was 0.3 meV for the HH and LH peaks, and 0.7 meV for the SO peak. Curves: Calculated results from Eqs. (1), (2) and parameters Δ_{SO} and Δ_{CF} fit to the experimental points

[6] and [7], and the binding energy results of [8], the GaInP binding energy was estimated for the three valence bands, and over the limited range of ordering in these samples. The results were constant to within $\pm 3\%$ which is within our experimental reproducibility. Therefore the measured exciton energy differences $E_{LH} - E_{HH}$, $E_{SO} - E_{HH}$, and $E_{SO} - E_{LH}$ are interpreted as the energy difference between zone-center valence bands, δE_{12}, δE_{13}, and δE_{23}, respectively. These values, from eight samples exhibiting various degrees of ordering, are plotted in Fig. 2 as a function of $E_g \equiv$ (bandgap $-$ binding energy), the useful experimental parameter. This is qualitatively similar to the results of [5].

Treating the CuPt ordering as a perturbation to the zinc-blende structure, the valence bands can be described by the so called quasi-cubic model [9, 3]. The three band-edge states are:

$$E_1 = a + \frac{\Delta_{CF}}{3} \,, \tag{1}$$

$$E_{2,3} = a - \frac{1}{2}\left(\Delta_{SO} + \frac{\Delta_{CF}}{3}\right) \pm \frac{1}{2}\left[\left(\Delta_{SO} - \frac{\Delta_{CF}}{3}\right)^2 + \frac{8\,\Delta_{CF}^2}{9}\right]^{1/2} \,, \tag{2}$$

where a is an averaged shift of the valence band, Δ_{CF} is the so called crystal-field-splitting parameter which is the valence-band splitting without the spin–orbit interaction, and Δ_{SO} is the spin–orbit interaction parameter, all taken to be quadratic functions of the degree of ordering.

For each sample, using Eqs. (1, 2) and the experimental results δE_{13} and δE_{23}, we can solve for Δ_{CF} and Δ_{SO}. In practice, we use a numerical solution of a Hamiltonian (similar to [10]) that includes strain and composition dependence of band structure due to the small deviation of the composition from its lattice-matched value $x_0 = 0.52$. Fig. 3 shows the bandgap reduction and Δ_{SO} versus Δ_{CF}. Δ_{SO} is nearly independent of the ordering in the order parameter range covered by this work, with a mean value of $\Delta_{SO} = 102.6 \pm 0.2$ meV.
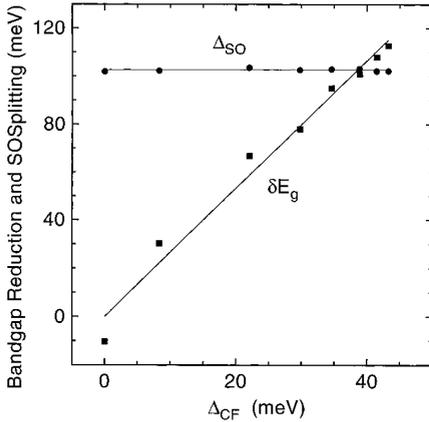
Fig. 3. Discrete points: extracted parameters from experimental data points. The SO splitting parameter and bandgap reduction are plotted against crystal-field splitting parameter. Bandgap reduction was referenced to a fitted value of $E_{HH} = 2003$ meV for the completely random material. Solid curves: linear fits to the data

The ratio $\delta E_g / \Delta_{CF}$ is found from Fig. 3 to be 2.66 ± 0.15. This deviates from the theoretical predictions, but it appears more close to the result of Mäder and Zunger [11] (pseudopotential in the local density approximation) than that of Wei et al. [3] (linearized augmented plane wave in the local density approximation). Plotted with our experimental data points in Fig. 2 are curves calculated using Eqs. (1), (2) with $\Delta_{SO} = 103$ meV and $\delta E_g / \Delta_{CF} = 2.66$ which have been obtained from Fig. 3.

In conclusion, for the first time DA is used for a systematic study of the valence-band and spin−orbit splitting in GaInP samples as a function of ordering. With the exceptions of our nominally random sample and the least ordered sample, the HH and LH peaks were always entirely separated from each other, with no need for a fitting procedure. Using the measured peak separations, we have made a quantitative investigation of the applicability of the quasi-cubic model to all the three valence bands, and studied the ordering effect on the spin−orbit interaction.

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