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The effects of diluted nitrogen impurities on the valence- and conduction-band states of $GaP_{1-x}N_x$ have been predicted and measured experimentally. The calculation uses state-of-the-art atomistic modeling: we use large supercells with screened pseudopotentials and consider several random realizations of the nitrogen configurations. These calculations agree with photoluminescence excitation (PLE) measurements performed for nitrogen concentrations x up to 0.035 and photon energies up to 1 eV above the GaP optical-absorption edge, as well as with published ellipsometry data. In particular, a predicted nitrogen-induced buildup of the L character near the valence- and conduction-band edges accounts for the surprising broad-absorption plateau observed in PLE between the X_{1c} and the Γ_{1c} critical points of GaP. Moreover, theory accounts quantitatively for the *downward* bowing of the indirect conduction-band edge and for the *upward* bowing of the direct transition with increasing nitrogen concentration. We review some of the controversies in the literature regarding the shifts in the conduction band with composition, and conclude that measured results at ultralow N concentration cannot be used to judge behavior at a higher concentration. In particular, we find that at the *high concentrations* of nitrogen studied here ($\sim$1%) the conduction-band edge (CBE) is a hybridized state made from the original GaP X_{1c} band-edge state plus all cluster states. In this limit, the CBE plunges down in energy as the N concentration increases, in quantitative agreement with the measurements reported here. However, at ultralow nitrogen concentrations ($\lesssim$0.1%), the CBE is the nearly unperturbed host X_{1c}, which does not sense the nitrogen cluster levels. Thus, this state does not move energetically as nitrogen is added and stays pinned in energy, in agreement with experimental results.

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GaP is an indirect-gap semiconductor with an X_{1c} conduction-band edge (CBE) located 0.5 eV below the Γ_{1c} direct-band edge. As shown in the 1960s,[1] minute amounts of nitrogen (10^{16} cm^{-3}) can create radiative levels in the gap below the CBE, due either to single-substitutional nitrogen or to nitrogen pairs ("cluster states"), which emit light. Recently, with the advent of molecular-beam epitaxy, it became possible to raise the alloy nitrogen concentration to a few percent (10^{20} cm^{-3}), thus introducing many more nitrogen clusters. This deeply affects the band structure of the mate-

tions considered theoretically in Ref. 17, the CBE is the nearly unperturbed host X_{1c}, which does not sense the localized nitrogen levels. Thus, this state does not move energetically as nitrogen is added, in agreement with the experiments reported in Ref. 19 for nitrogen concentration ranging from 0.008% to 0.1%. Finally, the theoretical prediction[18] of the existence of energy levels associated with N pairs much above the CBE is experimentally supported by the observation in PLE spectra of two weak and otherwise unexplained resonances.

[illegible]

$GaP_{1-x}N_x$ epilayers were grown by gas-source molecular-beam epitaxy on (001)-oriented GaP substrates. Nitrogen concentrations as determined by x-ray-diffraction measurements range from 0.24% to 3.5%. PLE measurements were taken at low temperature ($T=10$ K) by exciting the samples with a monochromatized tungsten lamp (spectral resolution equal to 2 nm). The luminescence was dispersed by a double 0.75-m-long monochromator and detected by a cooled photomultiplier with a GaAs cathode used in a single-photon-counting mode.

GaPN alloys were modeled by substituting a certain number of anion sites randomly chosen in (4□4□4) or (6□6□6) GaP supercells with nitrogen atoms. The atomic positions were relaxed by using the valence force-field method.[20] The electronic structure for a given alloy supercell was calculated fully atomistically by means of the empirical pseudopotential method[21] (EPM). Using exactly the same EPM parameters and codes[22,23] as were used previously in Refs. 17 and 18, the characterization of the GaPN random alloy states was extended up to 3.2 eV above the GaP valence-band

tion band edge is already a hybridized state involving the original GaP X_{1c} state and the nitrogen cluster-state levels. Such a hybridized alloy state—and not the $a_1(X_{1c})$ host state—plunges down in energy as the nitrogen concentration increases and eventually drops below the $e(X_{1c})$ host state, as shown here and in Refs. 17 and 18. As discussed in Ref. 17, such an *alloy*

0.3 eV *below* the valence-band maximum and up to 0.3 eV *above* the conduction-band minimum calculated at three different nitrogen concentrations, $x = 0.69\%$, 1.27%, and 3.47%. Here the random alloy was simulated in a 1728 atom (6 □ 6 □ 6)

ted lines in the figure). Since we are looking at the emergence of direct transitions [whose oscillator strength is much higher ($\approx 10^3$) than that for indirect transitions (see Ref. 27)], the choice of a square-root law to model the experimental (and calculated) absorption edges appears appropriate. However, we would like to point out that the fitting parameter E_g is a phenomenological parameter to which we will refer in the following as an *effective* optical-band gap. The experimental values of E_g are shown by open circles in Fig. 3(b).

The three different energy ranges investigated experimentally by PLE have been addressed theoretically as follows.

1. Lo -energ states belo the b lk GaP X_{1c} critical point and band gap bo ing

Figure 3(a) shows the intensity for optical-dipole transitions, as defined by Eq. (1), between all states down to

stead, the energy dependence of the dipole-matrix element squared as obtained by including transitions from states well below (down to 0.6 eV below) the top of the three valence bands. A Gaussian smearing of 0.02 eV is applied in all these plots.

In the "from VBM only" calculations of Fig. 4 the character of the conduction band in the energy region between the X_{1c} and $\Box_{1c}$ critical points shows a broad, featureless background plateau. Yet, the relative intensity in that region is much lower than that experimentally determined in PLE here, as well as in previous ellipsometry[10] and PLE measurements.[6–8] The agreement between experimental results and theoretical calculations is much better as soon as the role of additional optical transitions from the states below the VBM is taken into account (the solid lines in the figure). We conclude, therefore, that transitions *from below the VBM can contribute significantly to the optical-transition intensity*. This is especially important in the 2.5−3.2 eV region, where a significant buildup of the intensity takes place when the nitrogen concentration increases from 1.56% to 3.51%. This intensity is also relatively broadly spread, though somewhat inhomogeneously, with a bias skewed towards higher energies, a feature consistent with the observed PLE spectra.

by increasing the supercell size while keeping the N concentration fixed, as in Ref. 18.

The reasons for the increasing intensity of optical transitions from below the VBM are further clarified in Fig. 5 by the analysis of the distribution of □, *L*, and *X* character over the valence- (left panels) and conduction- (right panels) band edge vicinities. Therein, it can be recognized that the *L* character builds up near the conduction edge and starting from 0.3–0.4 eV below the valence-band edge and rapidly increases with *x*, in particular at 0.6 eV below the valence-band maximum. Thus, the featureless PLE background increasing with *x* in the X_{1c}-□$_{1c}$ energy region is due to transitions from below the VBM that are made possible by *the perturbation induced by nitrogen on the valence-band states*, a feature usually overlooked in previous theoretical investigations of III-N-V alloys.

3. High-energ states at and abo e the GaP Γ_{1c}

Present and previous PLE results, as well as ellipsometry data,[9,10] indicated that the E_0 transition in GaP, from the valence-band states to the □$_{1c}$ critical point, moves to higher energies, broadens, and gradually disappears with increasing *x*. This qualitative behavior is well described by our theoretical method.[18] In addition, the shift of the □$_{1c}$ critical point with nitrogen concentration is well reproduced by the present calculations. This is shown in Fig. 6, where theoretical results for the energy of the E_0 transition (full dots) agree rather well with the values experimentally determined by PLE in the present work (open circles) and by ellipsometry in Ref. 9 (open squares).

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Present and previous PLE measurements on GaPN epilayers having nitrogen concentration up to 3.5% have been compared with large-supercell empirical pseudopotential calculations of the electronic structures of random alloys. The large-supercell calculations reproduce the main features observed in the PLE spectra and provide new insights into the nature of those features. In particular, the calculations account quantitatively for the downward-moving conduction-band edge, and qualitatively for the increasingly large □ character of this edge. Moreover, a PLE background increasing with nitrogen concentration between the GaP X_{1c} and □$_{1c}$ critical points is explained by taking into account transitions from below the valence-band maximum, which are strongly affected by N insertion in the lattice. Similarly, some weak features observed in the PLE spectra in this energy region might be identified with excited levels of second-nearest-neighbor nitrogen pairs resonant with the conduction-band states, as predicted in Ref. 18. Finally, the blueshift and broadening of the □$_{1c}$ critical point observed in previous PLE and ellipsometry measurements is qualitatively and quantitatively accounted for.

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