Evolution of III-V Nitride Alloy Electronic Structure: The Localized to Delocalized Transition

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Addition of nitrogen to III-V semiconductor alloys radically changes their electronic properties. We report large-scale electronic structure calculations of GaAsN and GaPN using an approach that allows arbitrary states to emerge, couple, and evolve with composition. We find a novel mechanism of alloy formation where localized cluster states within the gap are gradually overtaken by aproximation" [1], the "coherent potential appro

[1], the "two-level anticrossing model" [3], $k \cdot p$ alloy models [4], or modeling the alloys as small "supercells" containing an   array of impurities [5].

In contrast to weakly perturbed alloy systems, one encounters a special group of isovalent alloys where the differences in properties of the host and impurity atoms are large enough that even   impurities create bound states in or near the fundamental band gap [6,7]. In such alloy systems (ZnS:Te, GaP:N, GaAses the CS appear   the fundamental band gapas a progression of narrow energy levels [6] associated with single impurities, impurity pairs, triplets, etc., whereas the PHS appear as sharp resonances ("virtual bound states") within the continua. Such alloy systems lack "majority representation" [2] wave vectors, as Bloch symmetry is lost. Since such strongly perturbing impurities introduce fundamentally new electronic levelsbou3.73r dobs76fpmodified.73r61(vhst.]TJT25.1)-42oectors,u2itro3do"yelsrity concentration increase remain at first fixed [11,15,16], and then the lines mysteriously disappear, one by one [11,15,16], as the effective mass reaches a maximum [12]. As the composition is increased further, the emission turns into a broad band [11,15,17] which has a rapid redshift vs composition (band gap bowing of ~ 20 eV in GaAsN) [5], an anomalously low temperature coefficient [10], and a peculiar saturation of the energy with applied pressure [3]. Such alloys cannot be described by models that neglect fluctuations [1] or multiband coupling [3,4].

We have developed a pseudopotential supercell technique [2] suitable for modeling strongly perturbed fluctuating alloys. A random alloy is described as a large (1000–14 000 atom) box of the host crystal onto which an arbitrary number of impurity atoms are randomly substituted, thus creating a natural statistical distribution of various impurity clusters [2]. Atomic positions are relaxed (via a classic force field) to their strain minimizing positions. The electronic structure of several randomly selected configurations is computed via an empirical pseudopotential approach, after applying (artificial) periodicity to the large box. This approach describes the evolution of alloy states in an unbiased manner as alloy fluctuations are fully retained. Furthermore, specific CS and PHS are not assumed [3], but emerge naturally; such states are permitted to interact and evolve with composition. Here we apply this approach to GaP$_{1-x}$N$_x$ and GaAs$_{1-x}$N$_x$, investigating how the discrete CS, located initially in the fundamental band gap, and the PHS located within the continua develop with composition. We find that (i) the CS located in the band gap do not interact sufficiently so as to broaden and form an "impurity band" made of a superposition of such nitrogen-induced states [12]. Instead, the energy of the CS remains relatively constant, while the PHS broaden,

move down in energy into the fundamental band gap, and overtake the CS one by one. (ii) Once the CS are swept by the PHS, the ensuing "amalgamation of states" forming the conduction band-edge exhibits   , as its low-energy tail is dominated by the just swept-in CS, whereas its higher-energy end consists of the more extended PHS. This localized-delocalized duality in the band edge leads to exciton localization in the tail states, Stokes shift between absorption (into PHS) and emission (from CS), blueshift of low-temperature photoluminescence (PL) with increasing temperature (due to thermal transfer of carriers from CS to PHS), and anomalous pressure dependence of the band gap (due to the weak pressure dependence of the CS, at the band edge, compared to the bulk). (iii) As the impurity concentration increases further, the amalgamated band-edge state broadens, the states delocalize, and the system turns into a conventional alloy with smoothly varying physical properties. These nitride systems thus illustrate a novel class of alloy behavior, which
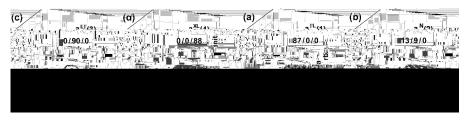
FIG. 2. Wave functions of the lowest energy a_1 conduction states of Ga<u>As</u>:N ($x_N \sim 0.05\%$). The x and y axes lie in the [100] and [010] directions, respectively.

high-order cluster states, spread throughout the upper part of the band gap hardly absorb light, but can be efficiently populated by tunneling from the higher-energy mobile PHS occupied optically. Thus CS are seen in PL, even though their concentration is low. This creates a Stokes shift between absorption and emission [11]. Furthermore, deeper CS appear in PL as the temperature is raised [10], when these levels are fed by cascading from the thermally populated higher-energy mobile states. The calculated pressure dependence of the pairs and cluster states in GaAs is $a_p = 20-60$ meV/GPa, while for the isolated N level $a_p = 40$ meV/GPa. These values are much reduced relative to the Γ_{1c} bulk value of 100 meV/GPa due to mixing of X_{1c} and L_{1c} character with much reduced a_p.

Calculations for GaP:N show similar behavior when compared to GaAs:N (Fig. 1), except that in the ultradilute limit (a) the $a_1(N)$ level is already inside the band gap at $E_c - 30$ meV, compared with the measured [6,9,13,14] E_c