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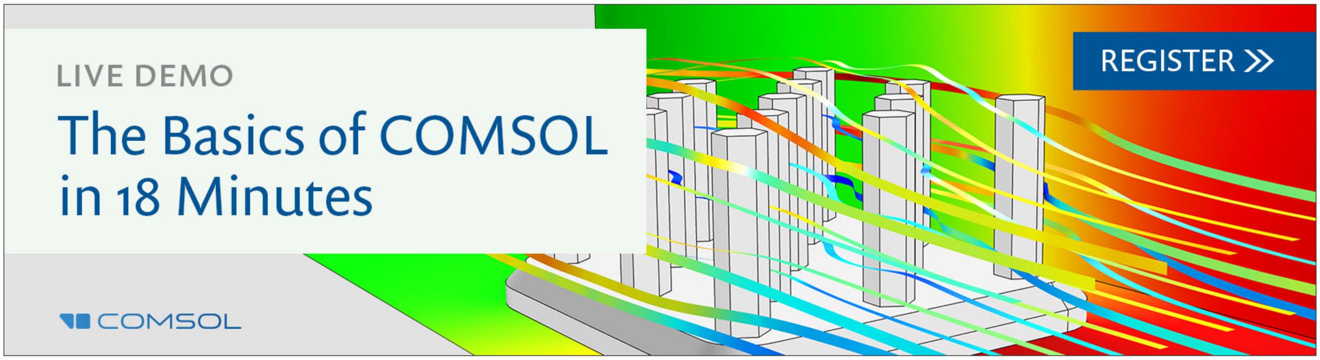

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Failure of nitrogen cluster states to emerge into the bandgap of GaAsN with application of pressure

P. R. C. Kent and Alex Zunger[a)]
National Renewable Energy Laboratory, Golden, Colorado 80401

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The electronic structure of GaAsN alloys was previously described in terms of nitrogen ''cluster states'' (CS) that exist in the dilute alloy in the bandgap, and ''perturbed host states'' (PHS) inside the conduction band. As the nitrogen concentration increases, the PHS plunge down in energy overtaking the CS. We show theoretically that the CS respond to the application of pressure in two different ways: the highly localized deep CS emerge (or remain) in the gap, because their pressure coefficient is lower than that of the conduction band minimum. In contrast, the shallow CS (first to be overtaken) hybridize so strongly with the conduction band that their pressure coefficient becomes comparable to that of the conduction states. These states fail to emerge into the gap upon application of pressure because they move, with application of pressure, at a similar rate with conduction states.

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The evolution of the electronic structure of III–V compounds upon addition of nitrogen has been recently clarified through theoretical modeling.[1–3] However, several important questions remain. We know that nitrogen introduces a strong perturbation into the III–V lattice, because of the significantly different atomic valence energy levels of N compared to P, As, and Sb, and also because the much smaller atomic size of N leads to strong atomic displacements.[4] The combined chemical and structural perturbation induces two types of electronic states in the nitride alloy.[1–3] First, the perturbed host states (PHS) represent mixing of the Γ-X-L and other conduction states by the nitrogen-induced perturbation. Second, cluster states (CS) are formed by single nitrogen atoms, nitrogen pairs[5] or trimers,[6] that are created randomly in the bulk, or because the alloy surface already has clusters[7] that are frozen-in during growth. At very low N concentrations, the CS occur inside the forbidden gap, whereas the PHS exist above the conduction band edge. At this very dilute limit, emission occurs from the CS, whereas absorption takes place to the PHS. The latter exhibit a low pressure coefficient[6,8] and heavy electron effective mass[9,10] due to inter-valley Γ-X-L mixing. Theory shows[4] that as the N concentration is increased, the CS remain narrow and pinned in energy, whereas the PHS rapidly move down in energy (''optical bowing'' created by the repulsion of the PHS by higher energy states). This situation is unlike the impurity band formation model[11] that predicts significant *broadening* of the CS and a *decrease* of the effective mass with concentration, both being contrary to observations.[9,10] Upon increasing the N concentration, the downwards moving PHS overtake one by one the CS, that become localized resonances above the conduction band edge. At this stage one observes the E_- conduction band edge and a more delocalized E_+ state above it, with an L-like E_* state[12] in between. Once the last CS state has been overtaken by the PHS, we encounter an ''amalgamated'' conduction band, made of resonant CS hybridized with PHS. This state exhibits characteristic temperature[13] and pressure dependencies.[14–16]

The properties of the amalgamated state are the subject of several recent inquiries.[4–14] An interesting question is to what extent localized and delocalized states are mixed. Klar *et al.*[14] found that upon application of pressure the conduction band edge is displaced to higher energies at a rapid pace, so the CS re-emerge into the gap. This reflects the low pressure coefficient of the CS, due to their weak hybridization with the PHS. Similarly, Buyanova *et al.*[16] found that quantum confinement of the GaPN alloy using a GaP barrier can displace the alloy conduction band edge to higher energies, again exposing the CS which are less prone to quantum confinement on account of their greater localization. One would expect that for sufficiently high N composition or sufficiently high-energy CS, the CS will strongly hybridize with the delocalized host states and become host-like. At this point they will acquire a similar degree of delocalization as the host. Upon application of pressure or quantum confinement, these states will *not* emerge into the band gap, but move with the conduction band edge. Encouraged by preliminary experiments by Weinstein *et al.*,[17] we have investigated theoretically the nature of the amalgamated states, so as to provide clear predictions for future experiments. In particular, we are interested in determining which CS are sufficiently hybridized so as not to emerge into the gap upon application of pressure, and which CS retain sufficient localization to emerge into the gap, on account of their lower pressure coefficient.

We have calculated the energy levels versus pressure of a supercell containing ~64 000 atoms with selected nitrogen clusters placed in it, using the plane-wave empirical pseudopotential method.[18] We consider two limiting nitrogen compositions: a highly dilute alloy where the CS are still in the gap, below the conduction band edge [Figs. 1(a) and 1(b)], and a well developed, postamalgamated alloy, where the CS have already been overtaken by the PHS and reside above the conduction band edge [Figs. 1(c) and 1(d)]. We apply pressure to both cases. We denote with ''D'' and ''L''

[a)] Electronic mail: alex_zunger@nrel.gov

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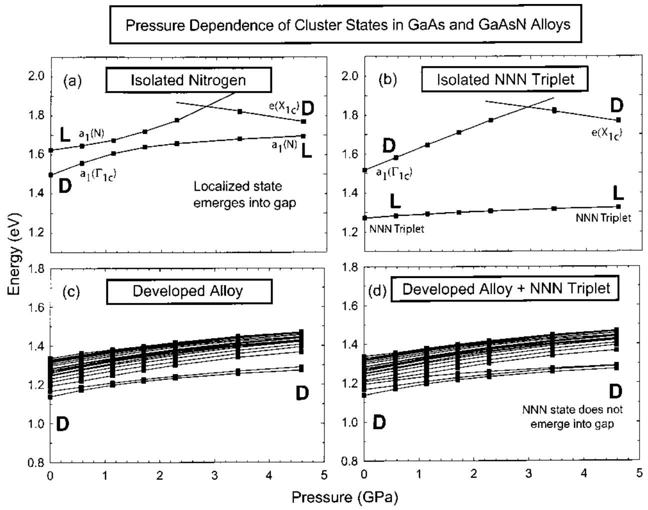

FIG. 1. Calculated pressure dependence of cluster states in GaAsN. D and L denote delocalized and localized states, respectively. (a) Isolated nitrogen in GaAs, (b) N–N–N triplet in GaAs, (c) the well-developed 1.5% GaAsN alloy, (d) the 1.5% alloy containing the N–N–N triplet.

whether the state is "delocalized" or "localized," respectively. The results are as follows:

(a) *Isolated nitrogen in the dilute limit*: In the highly dilute alloy, an *isolated* nitrogen impurity [Fig. 1(a)] appears at low pressure as a localized $a_1(N)$ level above the delocalized conduction band edge $a_1(\Gamma_{1c})$, as observed by Wolford *et al.*[19] and by Liu *et al.*[8] As pressure is applied, the $a_1(\Gamma_{1c})$ and $a_1(N)$ levels anti-cross, leading to the emergence of the localized $a_1(N)$ level into the gap, with its characteristically small pressure coefficient ($a_p = 12$ meV/GPa at P = ~4 GPa). The $\Gamma_{1c} - X_{1c}$ crossover, which occurs in pure GaAs at 4.3 GPa,[20] is displaced by the presence of N to higher pressures, outside the range of our present investigation. Figure 2(a) shows the wave function squared of the lowest conduction state of isolated N in GaAs. We see that this state becomes more localized with pressure, signifying the emergence of $a_1(N)$ into the gap.

(b) *Nitrogen triplet in the dilute limit*: As an example of a highly localized CS, we consider an N–N–N triplet in the C_{2c} geometry (a triplet of atoms aligned along the [110] axis). At low pressure this CS appears in the dilute alloy as an ultralocalized level, 250 meV below the conduction band edge [Fig. 1(b)]. As pressure is applied, the localized state remains in the gap: the delocalized conduction band edge moves rapidly to higher energies, whereas the triplet state moves with a very low pressure coefficient, owing to its highly localized character. Figure 2(b) shows the wave function squared of the isolated nitrogen triplet. We see that pressure does not change the degree of localization.

(c) *Impurities in well developed alloy*: A 1.5% random alloy [Fig. 1(c)] has various N clusters in it, which are formed by chance. In our example, the conduction band edge has now descended by 360 meV from the dilute limit [1.5 eV, Fig. 1(a), to 1.14 eV in the 1.5% alloy, Fig. 1(c)]. All CS are by now resonances above the conduction band edge, as evidenced by the fact that upon application of pressure [Fig. 1(c)] no states emerge into the band gap. To test this point specifically, we have deliberately placed in the well-developed alloy the same N–N–N triplet that produced a deep localized gap state in the ultradilute limit [Fig. 1(b)]. We find [Fig. 1(d)] that this state now lies in the conduction band. To probe if the NNN CS is localized or not, we apply pressure to this cell [Fig. 1(d)]. Inspection of the lowest 200 meV above the conduction band edge shows no ultralocalized state. We see that whereas in the dilute limit [Figs. 1(a)

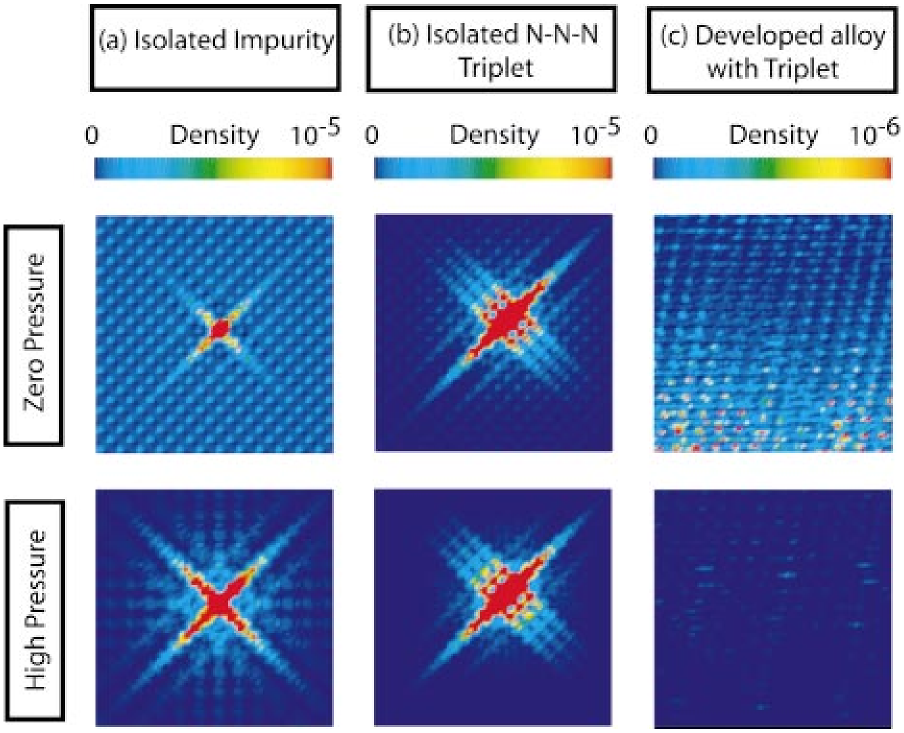

FIG. 2. (Color) The [001] cross sections of the wave function squared (density) of the lowest conduction state at zero and high (4.6 GPa) pressure of (a) isolated N in GaAs, (b) an isolated [110]-oriented nitrogen triplet in GaAs, (c) a well-developed 1.5% GaAsN alloy containing a [110]-oriented nitrogen triplet.

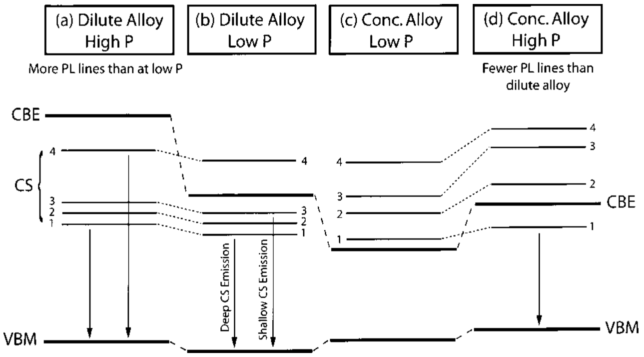

FIG. 3. Schematic description of the displacement of cluster states (CS) and conduction band edge in nitride alloys with pressure and composition. Note that upon application of pressure the shallow CS emerge (or stay) in the gap in the dilute alloy [(a),(b)], while in the concentrated alloy only the deepest CS emerge into the gap [(c),(d)].

and 1(b)] high pressure inevitably leads to the existence of a localized NNN level in the gap, in the strongly postamalgamated limit [Fig. 1(d)] the CS has sufficiently hybridized with the host conduction states that its pressure coefficient is no longer different from the host states. Consequently, all conduction states are displaced in energy in tandem, and no level emerges into the gap [Fig. 1(d)]. Figure 2(c) shows the wave function squared for the lowest conduction state of the developed alloy containing the nitrogen triplet. We see that at high pressure (~4.6 GPa) there is no localization.

We describe schematically, in Fig. 3, the pressure behavior of CS for dilute alloys [parts (a) and (b)], and concentrated alloys [(c) and (d)]. One can expect that there are intermediate cases between the ultradilute limit (where all CS exist in the gap at high pressure) and the well-developed alloy (no CS in the gap). In these intermediate cases the weakly hybridized CS, above but still close to the conduction band edge, e.g., state 1 in Fig. 3(c), will eventually emerge into the gap upon application of pressure (since their pressure coefficients are sufficiently distinct from those of the host conduction states). Thus the number of photoluminescence (PL) lines will *increase* with pressure [Fig. 3(a) versus Fig. 3(b)]. In contrast, the strongly hybridized CS that are further above the conduction band edge will not emerge into the gap upon application of pressure, e.g., states 2, 3, 4 in Figs. 3(c) and 3(d). We expect that the CS that are deepest in the dilute alloy [farthest below the conduction band edge, lowest energy PL], such as state 1 in Fig. 3(b), will be overtaken by the conduction band edge last, and thus re-emerge upon application of pressure, Fig. 3(d). The behavior illustrated in Fig. 3 contradicts the impurity band model[11] that suggests that the CS will broaden into a band at high nitrogen concentrations in GaAs. In this model it is assumed that above some concentration (⩽1% in GaAsN), all individual cluster states are lost because of mutual cluster–cluster interaction, which broadens these previously localized states. Consequently, in this model, application of pressure (which moves the CBM upwards) will either expose a broadband, or none at all. Both predictions contradict experiment. Our atomistic model predicts instead that the conduction band overtakes the *discrete* CS, so application of pressure can expose selectively localized CS, but fail to expose the conduction band hybridized CS.

Likewise the band anti-crossing model[21] does not predict the behavior illustrated, since the CS do not feature in this model altogether.

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