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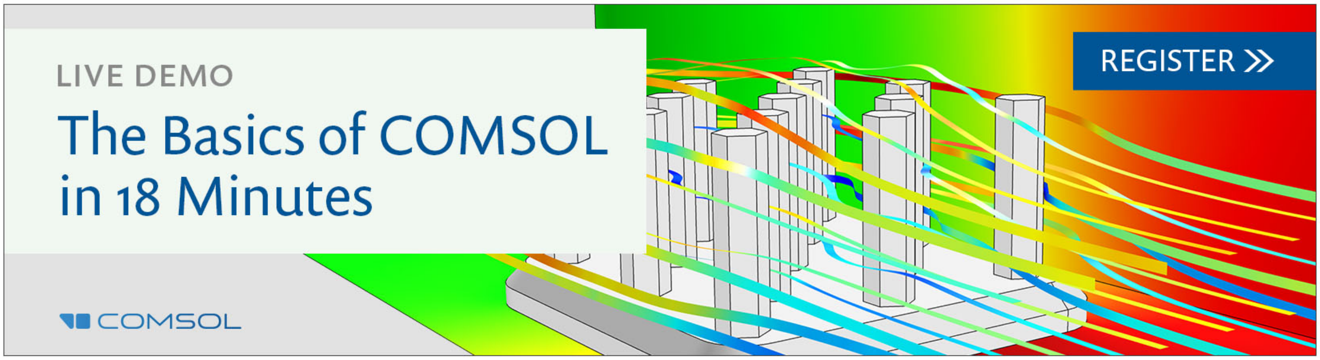

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Type I to type II transition at the interface between random and ordered domains of $Al_xGa_{1-x}N$ alloys

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We analyze the optical and transport consequences of the existence of ordered and random domains in partially ordered samples of $Al_xGa_{1-x}N$ alloys. Using atomistic empirical pseudopotential simulations, we find that the band alignment between random and ordered domains changes from type I to type II at $x \simeq 0.4$. This leads to an increase by two to three orders of magnitude in the radiative lifetime of the electron–hole recombination. This can explain the experimentally observed mobility-lifetime product behaviors with changing Al concentration. The type I to type II transition results from a competition between the ordering-induced band folding effect and hole confinement on Ga-rich monolayers within the ordered structure.
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During vapor-phase growth of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys,[1–5] long-range order develops, whereby the Ga and Al(In) atoms organize spatially on the two crystallographic sites of the wurtzite unit cell. The ordering is imperfect in two ways. First, the degree of long-range order η could be below the maximum value $\eta_{\max}(x)$, which depends on x via $0 \leqslant \eta \leqslant \eta_{\max}$, where $\eta_{\max}=1-|2x-1|$. Thus, for $x=0.5$ the maximum order corresponds to $\eta=1$, but lower homogeneous order, $0 \leqslant \eta \leqslant 1$, is possible too. Second, the ordering could be *inhomogeneous*, in that highly ordered domains are surrounded by unordered (random) alloy matrix, as observed experimentally in Refs. 3 and 6. Such an inhomogeneous ordering was predicted theoretically[7] to produce a larger band gap reduction for $Al_xGa_{1-x}N$ than what would be expected from equivalent homogeneous ordering. Here we investigate the consequences of the existence of *interfaces* between ordered domains and random-alloy domains on optical and transport properties of $Al_xGa_{1-x}N$ alloys. We use large supercell (~23 000 atoms) realizations of ordered-random domains, treated via atomistic empirical pseudopotential simulations. We find that the alloy is ''type I,'' with both holes and electrons localized on the ordered domains, as long as the Al concentration is below ~40%, or above ~90%. In the intermediate concentration range of 40%–90% Al the holes are localized on the random alloy domains, whereas the electrons are confined to the ordered domains. This type I to type II transition is accompanied by a sharp drop in the interband transition dipole matrix element. This could explain the experimental observation[6] that at Al concentrations $x \sim 0.4$–0.5 the mobility-lifetime ($\mu\tau$) product for $Al_xGa_{1-x}N$ is two orders of magnitude higher than for GaN ($x=0$) with the same resistivity, as being due to trapping of holes and electrons on different domains, as suggested by Misra *et al.*[6] We explain the type I to type II transition as being due to a competition between the enhanced hole localization on the Ga-rich layers of the ordered structure and ordering-induced ''band folding.''

To model ordered and random domains in $Al_xGa_{1-x}N$ alloys, we use a periodic sequence of $(11\bar{2}0)$-oriented[8] 40-monolayer (~12.6 nm) thick slabs of $Al_xGa_{1-x}N$ with order parameter $\eta_{\max}(x)$ alternating with 40-monolayer thick areas of $\eta=0$ $Al_xGa_{1-x}N$ random alloy. The simulation supercell covers 288 atoms (144 cation sites) within each $(11\bar{2}0)$ monolayer, with a total of 23 040 atoms per supercell. The electronic structure of such supercells is modeled fully atomistically via the empirical pseudopotential method,[9] with a pseudopotential $V(\mathbf{r})=\Sigma_{\alpha,n} v_\alpha(\mathbf{r}-\mathbf{R}_{\mathbf{n}\alpha})$ made of a superposition of screened atomic pseudopotentials (α=Ga,Al,N) situated on atomic sites $\mathbf{R}_{\mathbf{n}\alpha}$. Spin–orbit interaction is neglected. The atomic site positions are determined via relaxing the total elastic (valence force field[10,11]) energy of the supercell. Here the atomic pseudopotentials include explicitly local environment[12] and local strain[13] dependencies. The Hamiltonian $H=-\frac{1}{2}\nabla^2+V(\mathbf{r})$ is diagonalized in a plane-wave basis set via the folded spectrum method.[14] The atomic pseudopotentials for AlGaN system[7] are determined by requiring that the properties of bulk AlN and GaN are correctly reproduced. This includes (i) measured principal band gaps,[15] (ii) local density approximation (LDA) calculated crystal field splittings and AlN/GaN valence band offset,[16] (iii) GW-approximation quasiparticle band energies[17] at high symmetry points, (iv) measured band gap pressure coefficients,[18] and (v) LDA calculated absolute valence band volume deformation potentials[19] for zinc blend structure. The achieved quality of the fit is described in Ref. 7.

Figures 1(a) and 1(b) describe the band edge energies $\varepsilon_{\mathrm{VBM}}(x,\eta)$ and $\varepsilon_{\mathrm{CBM}}(x,\eta)$ of the homogeneously random alloy ($\eta=0$) and the homogeneously ordered alloy [$\eta=\eta_{\max}(x)$]. We see that for $x \lesssim 0.4$ (and $x \gtrsim 0.9$) the valence band maximum (VBM) energy is higher and the conduction band minimum (CBM) energy is lower on the ordered domain than on the random alloy domain, leading to a small ''type I'' offset with both electrons and holes residing on the ordered domains. This is evident from the plot of the CBM (electron) and VBM (hole) wave functions in Fig. 2(a), showing that both states are localized on the ordered domain. On the other hand, Fig. 1 shows that for $0.4 \lesssim x \lesssim 0.9$, the VBM of the ordered domain is *below* the VBM of the random alloy domain, whereas the CBM of the ordered domain is still below that of the random alloy domain. This corre-

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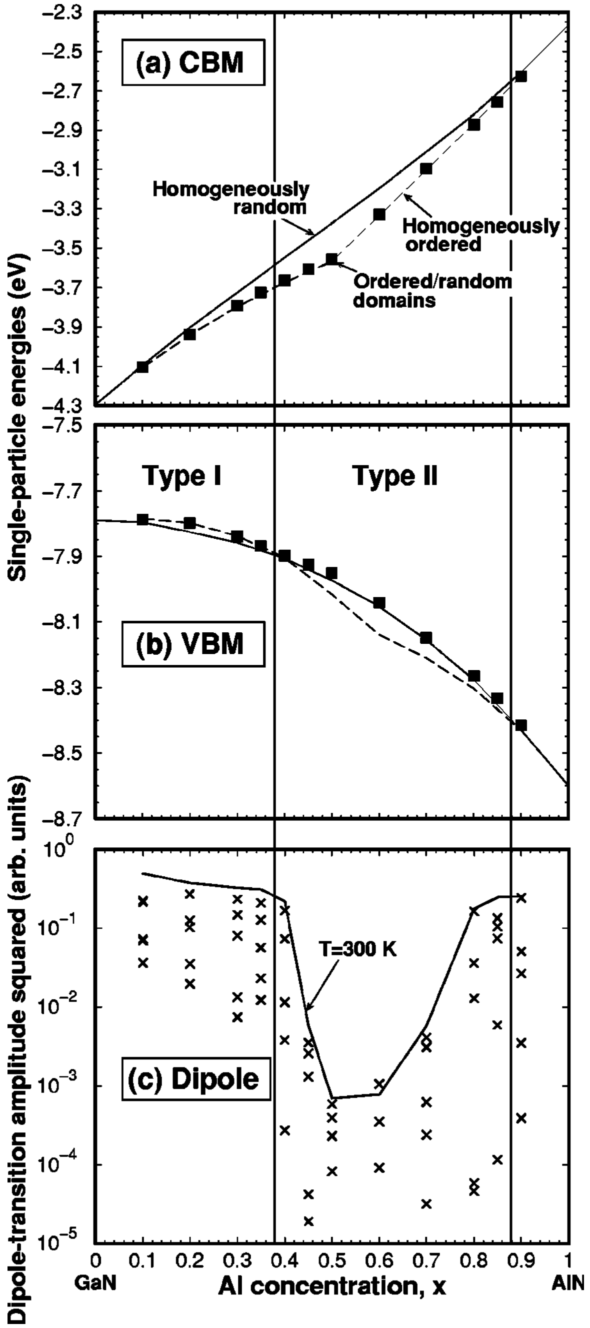

FIG. 1. (a) Conduction band minimum (CBM) and (b) valence band maximum (VBM) eigenenergies, as functions of Al concentration x for a system composed of ordered and random domains, in comparison with those for homogeneously random and homogeneously ordered [maximal ordering, $\eta = \eta_{\max}(x)$] alloy systems. The bottom panel (c) shows amplitudes squared of the dipole matrix transition elements between the CBM and the top five VBM states as a function of Al concentration (crosses). The solid line shows the Boltzmann average (using temperature $T = 300$ K) of the matrix elements squared for those five transitions at each concentration.

sponds to a "type II" offset with holes on the random alloy domain and electrons on the ordered domain. This is demonstrated by the wave function plot in Fig. 2(b), showing localization on different domains.

Consequences of the type I to type II transition: Figure 1(c) shows as crosses the dipole matrix element versus composition, for transitions between the top five valence band states and the CBM. A Boltzmann average of those transitions at temperature $T = 300$ K is shown as a solid line. While in the type I regime of $x \lesssim 0.4$ (and $x \gtrsim 0.9$) we see

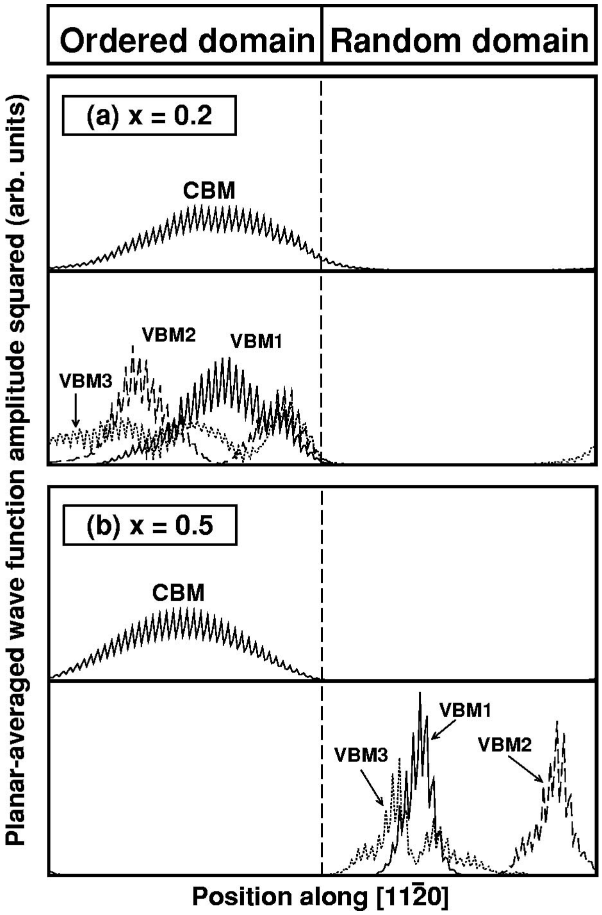

FIG. 2. Planar-averaged wave function squared perpendicular to the random/ordered interface for the CBM (for electrons) and the top three VBM (for holes) states of a system consisting of an interface between the random ($\eta = 0$) and ordered ($\eta = \eta_{\max}$) domains of an inhomogeneously ordered $Al_xGa_{1-x}N$ alloy. (a) $x = 0.2$, where electrons and holes are localized on the ordered domain ("type I"); (b) $x = 0.5$, where electrons are still localized on the ordered domain, but the holes are on the random alloy domain ("type II").

strong optical transitions, as expected, in the type II regime of $0.4 \lesssim x \lesssim 0.8$ the transition dipoles are two to three orders of magnitude weaker. Based on the Fermi golden rule in the dipole approximation, the radiative lifetime τ for VBM $\rightarrow$CBM transition (electron–hole recombination) is inversely proportional to the amplitude squared of the dipole matrix element for the same transitions [Fig. 1(c)]. Thus, the experimental behavior of the mobility-lifetime product ($\mu\tau$) measured in Ref. 6, showing a two to three orders of magnitude higher $\mu\tau$ for $x \simeq 0.4$–0.5 than for $x = 0$, for samples with the same resistivity, can be explained[20] as being due to a similar drop in the the dipole matrix amplitude squared due to a type I to type II transition.

Explanation of why the VBM of the ordered domain shifts below that of the random domain at $0.4 \lesssim x \lesssim 0.9$: The ordered $Al_xGa_{1-x}N$ alloy is an alternating sequence of two types of (0001) cation monolayers, which have different Al concentrations, one is Al-poor (concentration x_1) and the other is Al-rich (concentration x_2), with $x = (x_1 + x_2)/2$ and $\eta = x_2 - x_1$. As illustrated by Fig. 3(a), the maximal allowed difference $x_2 - x_1 = \eta_{\max}$, under the constraint of $x_{1,2} \geqslant 0$ grows with x for $x < 0.5$. It reaches $\eta_{\max} = 1.0$ at $x = 0.5$, and then decreases back to zero at $x > 0.5$. There are three physi-

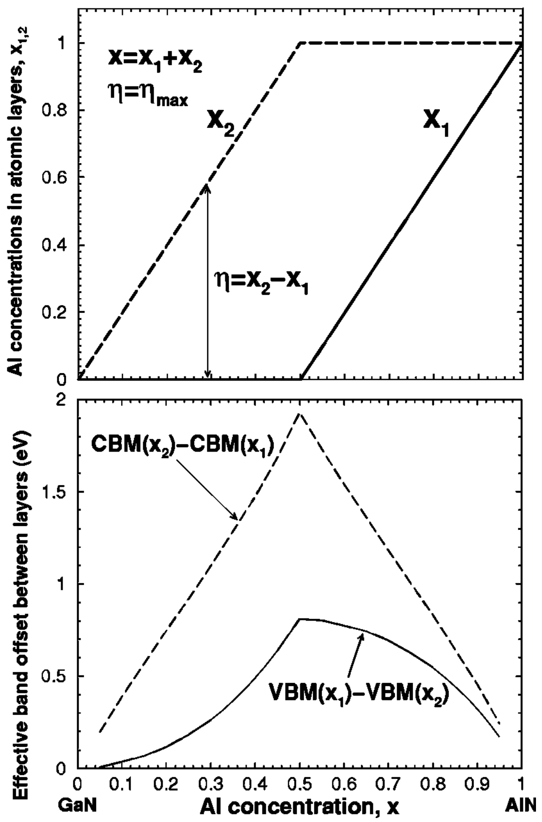

FIG. 3. (a) Different concentrations, x_1 and x_2, of Al atoms in two neighboring (0001) cation atomic layers in a maximally ordered alloy at a given total Al concentration x. (b) Effective band offsets between two neighboring cation layers for a maximally ordered alloy, assumed to be equal to the CBM and VBM band offsets between two totally random alloys with Al concentrations x_1 and x_2.

cal factors that control the energy of the VBM of the ordered domain.

(a) *Depth of quantum wells*: The effective band offset between the Al-rich monolayers x_2 and Al-poor (Ga-rich) monolayers x_1 within the ordered domain can be modeled as the potential offset between two random alloys with composition x_1 and x_2, and is shown in Fig. 3(b). The Al layer has a deeper VBM than the Ga-rich layers (much like in pure AlN/GaN heterointerfaces[16]). We see that in the "type I" region the offset is below 0.5 eV, whereas in the "type II" region the offset is larger than 0.5 eV.

(b) *Quantum confinement*: The offset between the monolayers of the ordered domains causes quantum confinement whereby the holes localized on the Ga-rich layers will be pushed to *deeper* energies, below the VBM of the random alloy.

(c) *Band folding*: Ordering causes the VBM $\overline{\Gamma}_{3v}(\Gamma_{5v})$ to be displaced to *higher* energies by repulsion from the lower-energy folded-in $\overline{\Gamma}_{3v}(\Gamma_{6v})$ state. If effect (a) is weak, i.e., small ($\lesssim 0.5$ eV) offset, then the quantum confinement effect (b) is also weak and effect (c) of band folding and repulsion wins, leading to the VBM of the ordered domain being *above* that of the random alloy. This is the case (Fig. 1) for $x \lesssim 0.4$ and $x \gtrsim 0.9$. If, on the other hand, effect (a) is strong, i.e., large ($\gtrsim 0.5$ eV) offset between the monolayers, then quantum confinement effect (b) is also strong, leading to the VBM of the ordered alloy being pushed *below* the VBM of the random alloy. This is the case (Fig. 1) for $0.4 \lesssim x \lesssim 0.9$.

In summary, we have predicted that domains of ordered and random $Al_xGa_{1-x}N$ alloys lead to localization of both electrons and holes on the ordered domains if x is below 40% or above 90%, but in the intermediate composition range the electrons are localized on the ordered alloy, whereas the holes are localized on the random alloy. This causes a sharp drop in the absorption intensity and electron–hole recombination rate. The transition to type II is caused by a large effective band offset between the Ga-rich and Al-rich layers of the ordered structure, so that quantum confinement (pushing the VBM of the ordered material below the VBM of the random alloy) dominates over the band folding effects.

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