Optical consequences of long-range order in wurtzite $Al_xGa_{1-x}N$ alloys

S. V. Dudiy and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401, USA
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The effect of 1:1 long range order on optical properties of $Al_xGa_{1-x}N$ alloys is investigated by means of first-principles calculations combined with large-scale atomistic empirical-pseudopotential simulations. We propose an intra-band mechanism of ordering-induced band gap reduction for different optical polarization. The scaling of band gap reductions with order parameter is analyzed. Our simulations of inhomogeneous ordering suggest that coexistence of ordered and random domains may explain the large magnitude of the observed redshifts upon ordering.

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Spontaneous CuPt ordering of otherwise random *zincblende* III-V semiconductor alloys[1] (e.g., $Ga_xIn_{1-x}P$) results in doubling of the unit cell into an alternate monolayer superlattice $(GaP)_1/(InP)_1$. This cell doubling folds *non*-Γ bands onto the Brillouin zone center, creating new optical transitions due to such inter-valley (e.g., Γ-L) coupling. The recent discovery of 1:1 long-range ordering in *wurtzite* III-V nitride alloys $AlGaN_2$ (Ref. 2) and In

axis along (0001)], whereas the Γ_{5v} states have $p_{x,y}$ character.[12,13] The different character of these valence states results in two different types of optical transitions at threshold: the *xy*-polarized $\Gamma_{1c} \leftrightarrow \Gamma_{5v}$ and the *z*-polarized $\Gamma_{1c} \leftrightarrow \Gamma_{1v}$, with different transition energies, $E_g^{(xy)}$ and $E_g^{(z)}$, respectively. Upon long-range ordering, the Γ_{1v} state of the wurtzite constituents AlN and GaN form the $\bar{\Gamma}_{1v}(\Gamma_{1v})$ state of ordered $AlGaN_2$, whereas the Γ_{5v} state of the wurtzite constituents form the $\bar{\Gamma}_{3v}(\Gamma_{5v})$ state of $AlGaN_2$ (we denote states of the ordered compound by bar, and indicate its parenthood in parentheses). The wurtzite structure also has a deeper valence state of Γ_{6v} symmetry (Fig. 1). This state creates upon ordering another $\bar{\Gamma}_{3v}(\Gamma_{6v})$ state. We see that valence band states of different symmetries (Γ_6 and Γ_5) in the constituent compounds have now formed states of the same symmetry—$\bar{\Gamma}_{3v}(\Gamma_{5v})$ and $\bar{\Gamma}_{3v}(\Gamma_{6v})$—in the ordered alloy. These states must now repel each other (''avoided crossing''), thus displacing the valence $\bar{\Gamma}_{3v}(\Gamma_{5v})$ state upwards. Figure 1 also shows that the Γ_{1c} and Γ_{3c} conduction states of the wurtzite constituents create, upon ordering, the equal-symmetry states $\bar{\Gamma}_{1c}(\Gamma_{1c})$ and $\bar{\Gamma}_{1c}(\Gamma_{3c})$. Such states must also repel each other, lowering the conduction band minimum (CBM). Thus, upon ordering, the upward shift of $\bar{\Gamma}_{3v}(\Gamma_{5v})$ will reduce the $\bar{\Gamma}_{3v} - \bar{\Gamma}_{1c}$ band gap, while the downward shift of $\Gamma_{1c}(\bar{\Gamma}_{1c})$ will reduce both the $E_g^{(xy)} = \bar{\Gamma}_{3v} - \bar{\Gamma}_{1c}$ and the $E_g^{(z)} = \bar{\Gamma}_{1v} - \bar{\Gamma}_{1c}$ gaps.

To evaluate the magnitude of the ordering-induced band gap reductions for $Al_{0.5}Ga_{0.5}N$ alloy, we perform first-principles calculations for AlN, GaN, ordered $AlGaN_2$, and random $Al_{0.5}Ga_{0.5}N$ modeled by special quasirandom structures (SQS),[14] using 16 and 32 atom supercells (SQS8 and SQS16).[14,15] We use the local-density approximation (LDA) (Ref. 16) for the exchange-correlation potential. The calculations are done with the VASP plane-wave pseudopotential code,[17] using projector augmented wave (PAW) potentials.[18] The Ga-*d* orbitals are included in the valence states. A 500 eV plane wave cutoff is used. The density of the *k*-point samplings is chosen to be close to that with 40 irreducible *k* points for a four-atom unit cell of wurtzite AlN or GaN. The lattice constant and c/a-ratio of the random alloy are fixed to the averages of the optimized AlN and GaN values, while allowing relaxation of all cell-internal atomic positions. All the structural parameters of the ordered phase are fully optimized. We do not include the small

valence band volume deformation potentials[33] for a zinc blende structure. The accuracy of the fit results compared to the target values is within 0.01 eV for principal band gaps; less than 0.001 eV for the crystal field splittings and valence band offsets; within around 0.1 eV for energies of Γ_{5v}, M_{1c}, M_{4v}, $A_{1,3c}$, $A_{5,6v}$, and $L_{1,3c}$ states; within 2% for Γ_{3c}, and within a few percent for K_{2c} and H_{3c}; within 2% for band gap pressure coefficients; and within 5% for valence band volume deformation potentials. With the present potential, a 1536-atom cell (and five configuration) calculation for random $Al_{0.5}Ga_{0.5}N$ alloy gives the band gap bowing coefficient of 1.06 eV, which is in the range 0.7–1.33 eV of recently measured values.[34] Our calculated effective masses are close, within around 30%, to measured electron effective masses[29] and non-spin-orbit LDA calculated hole effective masses,[35] while being systematically underestimated. The calculated band gap reductions are $\Delta E_g^{(xy)} = 0.19\,(0.17)$, $\Delta E_g^{(z)} = 0.11\,(-0.02)$, and $\Delta E_g = 0.15\,(0.09)$ eV, which are probably more accurate than the LDA values (in parentheses).

Figure 2 shows how the band gap of the $Al_{0.5}Ga($

in $(12-N_{\mathrm{ord}})$-layer thick random-alloy slabs ($\eta=0$). We use a $12\times12\times12$ supercell, consisting of 6912 atoms, averaging over three configurations. The averaged order parameter over supercell is defined as $\overline{\eta}=N_{\mathrm{ord}}/12$. Remarkably, already at $N_{\mathrm{ord}}=4$–7 ($\overline{\eta}=0.33$–0.58) the calculated band gap reduction (Fig. 3) is as large as 0.1–0.15 eV, approaching the maximal band gap reduction value of $\Delta E_g(1)=0.15$ eV. Thus, the existence of ordered and random domains can explain the observation of >0.1 eV band gap reductions for *partially* ordered, $\eta=0.3$–0.6, alloys, even though their values are close to $\Delta E_g(\eta=1)$. The η^2 and η^4 scaling laws of homogeneous ordering are not applicable in this case; thus simple extrapolations from $\eta=0.3$–0.6 to $\eta=1$ are unjustified.