Low In solubility and band offsets in the small-x $\beta$-Ga$_2$O$_3$/(Ga$_{1-x}$In$_x$)$_2$O$_3$ system

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Using first-principles calculations, we show that the maximum reachable concentration $x$ in the (Ga$_{1-x}$In$_x$)$_2$O$_3$ alloy in the low-x regime (i.e., the In solubility in $\beta$-Ga$_2$O$_3$) is around 10%. We then calculate the band alignment at the (100) interface between $\beta$-Ga$_2$O$_3$ and (Ga$_{1-x}$In$_x$)$_2$O$_3$ at 12%, the nearest computationally treatable concentration. The alignment is strongly strain-dependent: it is type-B staggered when the alloy is epitaxial on Ga$_2$O$_3$ and type-A straddling in a free-standing superlattice. Our results suggest a limited range of applicability of low-In-content GaInO alloys.

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increases steadily. For the configurations in Fig. 1 we find that the excess formation energies over that of a single In are \( \Delta E_f(2) = -0.044 \), \( \Delta E_f(3) = -0.019 \), \( \Delta E_f(4) = +0.021 \), \( \Delta E_f(5) = +0.074 \), \( \Delta E_f(6) = +0.144 \), and \( \Delta E_f(7) = +0.171 \), and \( \Delta E_f(8) = +0.180 \) in eV/In (the last two are not shown in the figure). The cell is kept at the volume of the undoped material, which is strictly correct in the dilute limit;\(^9,10\) at higher concentrations, we account for an enthalpic energy cost (see below). The concentration is evaluated as the thermal average of the In population in the supercell (\( M = 32 \) cation sites),

\[
x = \frac{\langle N \rangle}{M} = \frac{1}{M} \sum_{N=1}^{M} N \exp[-\beta E(N)],
\]

where \( \beta = 1/k_0 T \) and \( E(N) = E_f(1) + \Delta E_f(N) - T \delta S + \delta H \) is the free energy per In in the \( N \)-In substituted cell. \( E_f \) is the formation energy, \( S \) the formation vibrational entropy (we estimate it from the Debye temperature of the two bulk oxides, and find \( T \delta S \approx 0.15 \) eV), and \( \delta H \approx 0.09 \) eV is the energy cost related to the internal pressure building up in the constrained cell. \( \delta S \) is estimated as the energy difference (per In) between the constrained and volume-relaxed cell; if the cell length is allowed to change along a given direction, as would occur in epixy, \( \delta H \) decreases by about one third. In any event, as we have seen, entropy and enthalpy provide only small corrections over the structural energy \( E_f \) discussed above. The thermal population average given by Eq. (1) yields a concentration of 9%, with an error bar of +2 and −1% estimated by varying the \( \delta E \) values between 0.5 and 1.5 times those calculated. Again, this low solubility follows from the fact that tetrahedral sites are ruled out and In occupies only about 3 out of 16 octahedral sites in the cell on (thermal) average.

Having established the small solubility of In in Ga\(_2\)O\(_3\), we come to the band offsets. The correct way of calculating band offsets\(^9,10\) is as the sum \( \Delta E_b + \Delta V \) where \( \Delta V \) is the interface jump in electrostatic potential between the two regions being interfaced, and \( \Delta E_b \) is the difference between the band edge of interest in each of the two materials, each taken separately in its own internal potential. As mentioned, we use a \( 2 \times 2 \times 2 \) 160-atom cell, which is depicted in Fig. 2, upper panel, to describe the (100) interface: half of the supercell along the (100) axis is pure Ga\(_2\)O\(_3\), and the other half is a Ga-In alloy. We choose a concentration of 12% as it is near the maximum achievable (as discussed previously), and because, given the energetics constraints, the configurational freedom of In is very limited, and there is no serious need for detailed In configuration sampling, which would be computationally unfeasible. We choose the (100) interface for computational convenience; it remains to be assessed how much the offsets change with changes in the orientation.

This super-unit cell periodically repeats the two layers, effectively producing a superlattice; we find that the thickness of the layers is sufficient to reproduce identifiable bulk regions on either side of interface, with flat, bulk-like average potential, as shown in Fig. 2, lower panel. We study this superlattice in two strain states, epitaxial and free-standing; in the former case, we fix the lattice constants in the \( b-c \) crystal plane and the monoclinic angle at those of Ga\(_2\)O\(_3\) and relax the \( a \) lattice parameter; in the second case, we optimize all the lattice parameters. The internal coordinates are optimized in all cases.

As shown schematically in Fig. 3, at the (100) interface between Ga oxide and the alloy at 12% In, we find a type-B staggered alignment when the alloy is epitaxial on Ga\(_2\)O\(_3\) and a type-A straddling alignment in a free-standing superlattice. The valence offsets from Ga\(_2\)O\(_3\) to (Ga\(_{1-x}\)In\(_x\))\(_2\)O\(_3\) are \( -0.14 \) eV (Ga\(_2\)O\(_3\) epitaxial) and 0.15 eV (free-standing), and the conduction offsets are \( -0.41 \) eV (epitaxial) and \( -0.05 \) eV (free-standing). This considerable difference is due almost entirely to strain-induced shifts in the valence band maximum and conduction band minimum, whereas the electrostatic interface alignment is nearly insensitive to the strain. This indicates that a marked dependence on the strain state, and hence on the growth quality, is to be expected. Importantly, given the limited In solubility, this is about as much of an offset as can be expected between Ga\(_2\)O\(_3\) and (Ga\(_{1-x}\)In\(_x\))\(_2\)O\(_3\). There seems to be no measurement of the quantities just discussed, and we hope our prediction will stimulate work in this direction.

We expect the above estimate to be rather accurate. Our interface is between materials differing only very slightly owing to compositional changes, so beyond-DFT corrections to the band edges will essentially cancel out; on the other hand, strain-induced band-edge shifts are known to be described well by standard functionals.\(^11\) By the same token, in this case, the gap error also essentially cancels out, so the...
absolute value of the gap is immaterial to the offsets. For completeness, we mention that the GGA gap is about 2 eV, which is, as expected, a 60% underestimate compared to experimental values.\textsuperscript{1,12) Adding an empirical self-energy correction\textsuperscript{13,14) involving the calculated high-frequency dielectric constant, we obtain a gap of 4.2 eV, which is not far from the most recent experimental and theoretical beyond-DFT estimates of 4.6 and 4.7 eV, respectively, and will be discussed elsewhere.\textsuperscript{12) As reported previously,\textsuperscript{6) the gap rates of change with the composition and volume are also close to experimental values.\textsuperscript{1) In summary, we performed first-principles calculations of the bulk and interface properties of the Ga\textsubscript{2}O\textsubscript{3}/(Ga\textsubscript{1-x}In\textsubscript{x}) system. Importantly, we found that In is soluble in Ga\textsubscript{2}O\textsubscript{3} only up to a maximum of about 10%. The band offset between Ga oxide and the alloy at 12% In is type-B staggered when the alloy is epitaxial on Ga\textsubscript{2}O\textsubscript{3} and type-A straddling in a free-standing superlattice. The valence offsets from Ga\textsubscript{2}O\textsubscript{3} to (Ga\textsubscript{1-x}In\textsubscript{x})\textsubscript{2}O\textsubscript{3} are −0.14 eV (Ga\textsubscript{2}O\textsubscript{3} epitaxial) and 0.15 eV (free-standing), and the conduction offsets are −0.41 eV (epitaxial) and −0.05 eV (free-standing).

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