

Bond-length distribution in tetrahedral versus octahedral semiconductor alloys: The case of $\text{Ga}_{1-2x}\text{In}_x\text{N}$

L. Bellaiche, S.-H. Wei, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

Received 27 May 1997

Large (~ 1000 atoms) supercell valence force-field simulations are used to investigate the nearest-neighbor bond-length distribution in relaxed tetrahedral \sim zinc blende and wurtzite and octahedral \sim rocksalt $\text{Ga}_{1-2x}\text{In}_x\text{N}$ alloys. We find that, due to the rigidity of the octahedron, the distribution of each anion-cation bond length in *rocksalt alloys* has two contributions: unrelaxed bonds and relaxed bonds. These two peaks have a large width and overlap slightly, leading to a broad nearest-neighbor distance distribution. On the other hand, the anion-cation nearest-neighbor distribution in *zinc-blende alloys* can be decomposed into a sum over four closely spaced and sharp peaks associated with different clusters, leading to a narrow, single-peaked nearest-neighbor distribution. Finally the wurtzite alloys exhibit bond-length distributions that are very similar to the corresponding ones in the zinc-blende alloys, leading to a nearly identical strain energy in random zinc-blende and wurtzite alloys. ©0163-1829-97!04045-9#

I. INTRODUCTION

When an $A_{1-x}B_xC$ alloy is formed from lattice mismatched constituents AC and BC , its lattice constant $a(x)$ tends to be close to the composition-weighted average values \sim Vegard's rule, but the individual bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ remain distinct.^{1,2} This tendency has been studied extensively for *zinc-blende alloys*, and is now well understood in terms of atomistic relaxation models.²⁻¹¹ In these models, atoms are displaced from their lattice sites so as to minimize the strain energy that results from the difference between the actual bond lengths R_{AC} and R_{BC} and the ideal bond lengths R_{AC}^0 and R_{BC}^0 , as well as from the difference between the actual bond angles Q and the ideal \sim e.g., tetrahedral bond angle Q^0 . Due to the topological frustration of common crystal configurations,¹² a complete relaxation to reach *both* ideal bond lengths and ideal bond angles is usually not possible. In fact, there are only two ordered adamantine structures, where diamondlike constituents can attain the ideal bond configurations—the zinc-blende structure and the RH1 structure.¹² Thus, in general, the alloy system relaxes into a “compromise structure,” exhibiting a *distribution* of bond lengths and angles around the ideal values. Experimental measurements^{1,2} show that zinc-blende alloys exhibit bimodal anion-cation bond-length distribution, with only one type of $A-C$ bond and only one type of $B-C$ bond. Furthermore, experiment shows that with respect to the bond lengths R_{AC}^0 and R_{BC}^0 of the end-point constituents, if $R_{BC}^0 > R_{AC}^0$ then $R_{AC}(x) > R_{AC}^0$ and $R_{BC}(x) < R_{BC}^0$.

In this paper we investigate the magnitude and distribution of bond lengths in *rocksalt* and *wurtzite* alloys and compare them with the corresponding quantities in zinc-blende alloys. Our interest in rocksalt alloys stems both from recent measurements on such systems,¹³⁻¹⁶ and from an interesting geometric difference between a tetrahedral alloy and an octahedral alloy that could have a consequence on bond-length distribution. To see this difference, note that when A and B atoms \sim “mixed sublattice”!

distribution and a strain energy nearly identical between zinc-blende and wurtzite alloys. Hence, the ground state of the alloy is the same as that of its constituents.

**II. ANALYSIS OF BOND-LENGTH DISTRIBUTION
IN OCTAHEDRAL vs TETRAHEDRAL ALLOYS:
A SIMPLE MODEL**

$$P_{BC}^{j=2} \sim$$

general, four peaks for each bond. For the rocksalt alloys we found that the unrelaxed bond peaks ($j=1$) occur exactly at the position given by Eqs. 3 and 5, while the relaxed bond peaks ($j=2$) occur at a position differing by less than 0.03 \AA from its values given by Eqs. 3 and 5. This small discrepancy between the simulated results and the analytical predictions reflects the competition between the bond stretching and bond bending absent in our analytical model. Furthermore, the broadening of the simulation peaks relative to the analytical expectations of a single value for each type of bond length (see Eqs. 3 and 5) is partly due to this competition and partly due to higher-order terms which are also neglected in the analysis of Sec. II. On the other hand, the integrated peak probabilities of the two types of Ga-N and In-N bonds are *exactly* those given by Eqs. 4 and 6.

For the tetrahedral zinc-blende alloys, the simulated peaks positions differ once again slightly (by less than 0.03 \AA) from their simple predictions (Eqs. 7 and 8), while the integrated probability follows exactly Eqs. 7 and 8.

B. Relaxed cation and anion sublattices: Rocksalt vs zinc blende vs wurtzite

We now study the effect of the cation sublattice relaxations, as well as the anion sublattice relaxations on the bond-length distribution. Figure 3 shows the bond-length distribution in rocksalt and zinc-blende $\text{Ga}_{1-x}\text{In}_x\text{N}$ alloys, for $x =$

leading to a sharp bond-length distribution appearing single-peaked. Furthermore, the integrated intensity is equal to x for the In-N bond, and to $(1-x)$ for the Ga-N bond, as it should be at composition x . We can also define the *weighted average* nearest-neighbor Ga-N bond length as

$$\bar{R}_{\text{Ga-N}} = \frac{1}{m} \sum R_{\text{Ga-N}}^i, \quad \sim 10!$$

where the sum runs over the m different Ga-N bonds $R_{\text{Ga-N}}^i$ existing in the histograms displayed in Fig. 2 or 3. A similar definition holds for the *weighted average* nearest-neighbor $\bar{R}_{\text{In-N}}$ bond length. For each composition, we find that $\bar{R}_{\text{Ga-N}}$ and $\bar{R}_{\text{In-N}}$ in cation- and anion-relaxed zinc-blende alloys are almost equal (by less than 0.025 Å) to the corresponding weighted average bond lengths in cation-unrelaxed zinc-blende alloys.

On the other hand, as shown in Figs. 3-a)–3-c) the distributions of the different Ga-N (or In-N) bond lengths in *rock-salt*

$$D^{ZB-WZ}(x) = x(E_{\text{InN}}^{\text{ZB}} - E_{\text{InN}}^{\text{WZ}}) + (1-x)(E_{\text{GaN}}^{\text{ZB}} - E_{\text{GaN}}^{\text{WZ}}), \quad (12)$$

is +11 meV/atom at $x=0.5$,²⁵ while the formation energy difference $DH_{\text{ZB}} - DH_{\text{WZ}}$ is -20 meV/atom for $x=0.5$. Thus, their results suggest that for the 50%-50% alloy, the zinc-blende phase is *more stable* than the wurtzite phase by around $20 - 11 = 9$ meV/atom!, despite the fact that the end-point constituents prefer the wurtzite structure by 11 meV/atom.²⁵ To test whether such an alloy stabilized zinc-blende phase of $\text{Ga}_{0.5}\text{In}_{0.5}\text{N}$ can be obtained, we have computed, via the VFF approach DH_{ZB}^{32} and DH_{WZ}^{32} using the same 32-atom supercells as in Ref. 17. We found for $\text{Ga}_{0.5}\text{In}_{0.5}\text{N}$: $DH_{\text{ZB}}^{32} = 36$ meV/atom and $DH_{\text{WZ}}^{32} = 55$ meV/atom. The VFF energy difference -19 meV/atom, and is thus similar to the LDA energy 5730 TD