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Predicted bond length variation in wurtzite and zinc-blende InGaN and AlGaN alloys

T. Mattila^{a)} and Alex Zunger^{b)}

National Renewable Energy Laboratory, Golden, Colorado 80401

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Valence force field simulations utilizing large supercells are used to investigate the bond lengths in wurtzite and zinc-blende $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ random alloys. We find that ~i! while the first-neighbor cation–anion shell is split into two distinct values in both wurtzite and zinc-blende alloys ($R_{\text{Ga-N}_1} \neq R_{\text{In-N}_1}$), the second-neighbor cation–anion bonds are equal ($R_{\text{Ga-N}_2} = R_{\text{In-N}_2}$). ~ii! The second-neighbor cation–anion bonds exhibit a crucial difference between wurtzite and zinc-blende binary structures: in wurtzite we find *two* bond distances which differ in length by 13% while in the zinc-blende structure there is only *one* bond length. This splitting is preserved in the alloy, and acts as a fingerprint, distinguishing the wurtzite from the zinc-blende structure. ~iii! The small splitting of the first-neighbor cation–anion bonds in the wurtzite structure due to nonideal c/a ratio is preserved in the alloy, but is obscured by the bond length broadening. ~iv! The cation–cation bond lengths exhibit three distinct values in the alloy ~Ga–Ga, Ga–In, and In–In!, while the anion–anion bonds are split into two values corresponding to N–Ga–N and N–In–N. ~v! The cation–related splitting of the bonds and alloy broadening are considerably larger in InGaN alloy than in AlGaN alloy due to larger mismatch between the binary compounds. ~vi! The calculated first-neighbor cation–anion and cation–cation bond lengths in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy are in good agreement with the available experimental data. The remaining bond lengths are provided as predictions. In particular, the predicted splitting for the second-neighbor cation–anion bonds in the wurtzite structure awaits experimental testing. © 1999 American Institute of Physics. @S0021-8979-99!09601-2#

I. INTRODUCTION

The lattice constant $a(x)$ of an isovalent $A_xB_{1-x}C$ semiconductor alloy, formed by constituents AC and BC , is known¹ to closely follow the composition-weighted average between the binary endpoints ~Vegard’s rule!. In contrast, the nearest-neighbor bond lengths, $R_{A-C}(x)$ and $R_{B-C}(x)$ exhibit, in general, distinct values, resembling more their values in the individual binary constituents AC and BC rather than an average value corresponding to the virtual-crystal limit.²⁻⁵ For alloys made of zinc-blende ~ZB! constituents this has been explained theoretically using atomistic relaxation models.³⁻⁸ For the alloys made of wurtzite ~W! constituents, such as the III–V nitride alloys ~InGaN, AlGaN, etc.!, only very recent theoretical predictions⁹ and experimental measurements¹⁰ of the bond lengths have become available. The ground state of bulk-grown AlN, GaN, and InN is the W structure.¹¹⁻¹³ However, epitaxial stabilization¹⁴ of ZB phase is possible.^{11,12}

There are two significant, ~and often overlooked! structural differences between the bond distances in ZB and W structures of binary compounds:

~i! The ZB structure has only one type of first-neighbor distance

$$R_{A-C}^{zb} = \frac{A_3}{4} a_{zb} \quad \text{~four bonds!}, \quad \sim 1!$$

where a_{zb} denotes the ZB lattice parameter, yet the W structure has *two* types of first-neighbor anion–cation bond distances ~see Fig. 1!:

$$R_{A-C}^w = u \frac{c}{a_w} a_w \quad \text{~one bond!} \quad \sim 2!$$

$$R_{A-C_{2a}}^w = \sim 1 - u! \frac{c}{a_w} a_w \quad \sim \text{one bond!}$$

R

constants, derived from first-principles calculations,¹⁷ are given in Table I. Also given in Table I are the input ideal bond lengths (d^0). In the alloys, we use the arithmetic mean for the bond bending $\sim b!$ force constants for bond angle

TABLE III. Comparison of the relaxed bond lengths \sim in angstroms! in zinc-blende $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy as calculated using three methods: \sim V! Relaxing atomic positions while keeping the lattice parameter fixed to the value given by Vegard's rule, \sim R! relaxing the lattice parameter in addition to atomic positions, and \sim S! like V but scaling the bond lengths by the change $d(x)$ in lattice parameter. $d(x)$ equals -0.39% for $x=0.50$, and -0.30% for $x=0.25$ or 0.75 .

x	Method	$R_{\text{Ga-N}_1}$	$R_{\text{In-N}_1}$	$R_{\text{Ga-N}_2}$	$R_{\text{In-N}_2}$	$R_{\text{Ga-Ga}}$	$R_{\text{Ga-In}}$	$R_{\text{In-In}}$	$R_{\text{N-N}_a}$	$R_{\text{N-N}_b}$
0.25	V	1.9633	2.1255	3.8311	3.8385	3.2428	3.2964	3.3208	3.2039	3.4707
0.25	R	1.9574	2.1195	3.8198	3.8271	3.2331	3.2869	3.3108	3.1943	3.4609
0.25	S	1.9574	2.1191	3.8196	3.8270	3.2330	3.2865	3.3109	3.1943	3.4603
0.50	V	1.9730	2.1408	3.9259	3.9398	3.2965	3.3549	3.4050	3.2176	3.4955
0.50	R	1.9651	2.1327	3.9106	3.9244	3.2832	3.3419	3.3918	3.2046	3.4823
0.50	S	1.9653	2.1324	3.9106	3.9245	3.2836	3.3418	3.3918	3.2050	3.4818
0.75	V	1.9783	2.1511	4.0198	4.0354	3.3371	3.4124	3.4650	3.2275	3.5108
0.75	R	1.9721	2.1449	4.0080	4.0235	3.3266	3.4023	3.4549	3.2175	3.5006
0.75	S	1.9723	2.1446	4.0077	4.0233	3.3271	3.4022	3.4546	3.2178	3.5003

traction in lattice parameter $d(x)$ @Eq. \sim 7!#. We see that the bond lengths obtained using method S reproduce very accurately the bonds with method R \sim the differences occur in the fourth decimal!. In other words, the ratio between the bond lengths in calculations V and R is the same as the ratio between the lattice parameters in the two calculations. This indicates that allowing the lattice constant to relax does not lead to significant structural changes in the system but the change is directly propagated into bond lengths and the relative lengths of different bonds remain the same. Therefore, in the following we will use Vegard's rule to extract bond length values. To account for deviation from Vegard's rule, all bond lengths in Table IV can be multiplied by $d(x)$ of Eq. \sim 7!.

B. First-neighbor cation-anion bonds:
 $R_{A-C_{1a}}^w$ vs $R_{A-C_{1b}}^w$

Figure 2 compares the first-neighbor cation-anion bonds in the W $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ alloy as calculated using the two VFF models described in Sec. II. Figure 2-a! corresponds to the

VFF calculation assuming ideal c/a ratio @method \sim A!#, while Fig. 2-b! shows the result for nonideal c/a @method \sim B!#. In Fig. 2-b! we decompose the nearest-neighbor bond length distribution ($R_{A-C_1}^w$) into bonds parallel to the W c axis ($R_{A-C_{1a}}^w$) and perpendicular to it ($R_{A-C_{1b}}^w$). The decomposed bond lengths indicate that for both cation species the $R_{A-C_{1a}}^w$ bond is slightly longer than $R_{A-C_{1b}}^w$. However, this distinction is not visible in the combined $R_{A-C_1}^w$ bond distribution \sim the uppermost of the three histograms for each cation species in Fig. 2!. Thus, we conclude that the difference between $R_{A-C_{1a}}^w$ and $R_{A-C_{1b}}^w$ bonds is preserved in the alloy environment, but simultaneously becomes obscured due to the statistical bond length broadening.

We further note that the R_{A-C_1} peak positions do not coincide between Figs. 2-a! and 2-b!. The calculated average peak positions for the ideal \sim nonideal! c/a ratio are $R_{\text{Ga-N}_1} = 1.973$ (1.974) Å and $R_{\text{In-N}_1} = 2.141$ (2.132)Å, respectively. These differences can be understood as a consequence of the ideal \sim VFF! bond lengths assumed in methods \sim A! and

TABLE IV. Calculated values of the histogram \sim Fig. 3! average relaxed bond lengths \sim in angstroms! in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy for various compositions. The experimental values are from Ref. 10. For W structure an ideal c/a ratio is assumed in the calculations.

x	Structure	$R_{\text{Ga-N}_1}$	$R_{\text{In-N}_1}$	$R_{\text{Ga-N}_{2a}}$	$R_{\text{Ga-N}_{2b}}$	$R_{\text{In-N}_{2a}}$	$R_{\text{In-N}_{2b}}$	$R_{\text{Ga-Ga}}$	$R_{\text{Ga-In}}$	$R_{\text{In-In}}$	$R_{\text{N-N}_a}$	$R_{\text{N-N}_b}$
0.0	W	1.949		3.248	3.732			3.183			3.183	
0.0	ZB	1.949		3.732	3.732			3.183			2.183	
0.0	Exp.	1.94						3.19				
0.25	W	1.963	2.126	3.339	3.831	3.322	3.839	3.243	3.297	3.317	3.204	3.471
0.25	ZB	1.963	2.126	3.831	3.831	3.838	3.838	3.243	3.296	3.321	3.204	3.471
0.25	Exp.	1.94	2.09					3.25	3.275	3.35		
0.50	W	1.973	2.141	3.427	3.928	3.413	3.938	3.300	3.355	3.401	3.218	3.496
0.50	ZB	1.973	2.141	3.926	3.926	3.940	3.940	3.296	3.354	3.405	3.218	3.495
0.50	Exp.	1.96	2.12					3.30	3.355	3.40		
0.75	W	1.978	2.151	3.514	4.022	3.503	4.035	3.343	3.413	3.464	3.227	3.511
0.75	ZB	1.978	2.151	4.020	4.020	4.035	4.035	3.337	3.412	3.465	3.228	3.511
0.75	Exp.	1.96	2.12					3.35	3.395	3.46		
1.0	W		2.156			3.593	4.128			3.521	3.521	
1.0	ZB		2.156			4.128	4.128			3.521	3.521	
1.0	Exp.		2.15							3.53		

~B! ~Sec. II!

neighbor bond lengths.² However, the *average* anion position stays ideal. Therefore, the $R_{\text{Ga-N}_2}$ and $R_{\text{In-N}_2}$ exhibit nearly an equal value which coincides with the value in unrelaxed alloy.

The third and fourth columns in Table IV show the second-neighbor cation–anion bond lengths for the investigated $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy compositions. These values are graphically presented in Fig. 4-b! for the W structure. We again note the splitting between the $R_{A-C_{2a}}^w$ and $R_{A-C_{2b}}^w$ bonds, as well as the almost negligible cation dependence of the bond lengths. It is also evident that these second-neighbor cation–anion bonds have a stronger dependence on the alloy composition than the nearest-neighbor bonds $R_{\text{Ga-N}_1}$ and $R_{\text{In-N}_1}$. Currently, there are no experimental data available for the second-neighbor cation–anion bonds and the values in Table IV and Fig. 4-b! are offered as prediction.

F. Cation–cation and anion–anion bonds

The Ga–Ga, Ga–In, and In–In bonds shown in Fig. 3 exhibit three distinct values: the smallest distance is found for the Ga–Ga bond while In–In is the largest, and Ga–In between the two extremes. These three values are explained by the differing atomic radii of the cations. Both W and ZB structures exhibit nearly the same cation–cation bond lengths as shown in the fifth column in Table IV. The comparison between the calculated and experimental¹⁰ values in Fig. 4-c! indicates good agreement. We also note that the dependence on the alloy composition for the cation–cation bonds is significantly larger than for the nearest-neighbor bonds in Fig. 4-a!.

In the N–N bond distribution ~

ratio between these types of bonds in the W structure @see Eq. ~4!#. Therefore it might be overlooked in experiments with finite resolution or may be incorrectly assigned to an alloy-broadened part of the second-neighbor bonds. However, as Eq. ~4! shows, the existence of a *split* second-neighbor cation-anion bond is an intrinsic property of the W structure, and already exists in pure compounds, irrespective of c/a and u .

E. Second-neighbor cation–anion bonds:

R_{A-C_2} vs R_{B-C_2}

Figures 3-a! and 3-b! show that the $R_{\text{Ga-N}_2}$ and $R_{\text{In-N}_2}$ distances have nearly identical ~cation independent! values in both W and ZB structures. This is in contrast with the first-neighbor distances $R_{\text{Ga-N}_1}$ and $R_{\text{In-N}_1}$ exhibiting distinct values. Rather, the effect of the alloy environment can be seen in the widths of the peaks which are much broader than for the peaks corresponding to first-neighbor cation–anion distances.

The distinction between first- and second-neighbor cation–bonds can be understood by considering the relative cation and anion displacements during alloy relaxation: to first order, cations ~Ga and In! remain at their ideal fcc-lattice positions while anions ~N! are displaced from their ideal sublattice sites in order to accommodate the nearest-

small differences between the anion–anion bond lengths between W and ZB alloys. The graphical illustration in Fig. 4-d! indicates again a linear dependence of the anion–anion bond lengths of the W alloy composition, with a slope similar to second-neighbor cation–anion bonds @Fig. 4-b!#.

We note that qualitatively similar behavior of cation–cation and anion–anion bonds ~slopes, splitting of the anion–anion bonds! has been observed in zinc-blende InGaAs alloys.^{5,8,19}

IV. BOND LENGTHS IN $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ALLOY

The bond length distribution for W $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ alloy is shown in Fig. 5. In comparison with $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ ~Fig. 3! we note that the distribution peaks are much sharper, as expected based on the smaller lattice mismatch between AlN and GaN alloys. Also, the splitting between, e.g., $R_{\text{Ga-N}_1}$ and $R_{\text{Al-N}_1}$ is much smaller than in $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$. Otherwise, $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ alloy qualitatively reproduces all the essential features predicted for $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ above. Table V shows the predicted bond lengths for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy for $x=0,0.5,1$. We see that due to smaller lattice mismatch between AlN and GaN than InN and GaN the bond length dependence on the alloy composition is much smaller than in InGaN.

V. CONCLUSION

We have investigated the bond lengths in W and ZB InGaN and AlGaN alloys using the VFF simulations and large (512–1280 atom! supercells).

Our results show that while the first-neighbor cation–anion bonds for *different cations* (R_{A-C_1} and R_{B-C_1}) retain distinct values in the studied W and ZB alloys, the second-neighbor cation–anion bonds R_{A-C_2} and R_{B-C_2} merge into a single bond length. However, the second-neighbor cation–anion bonds for the *same cation* exhibit a crucial difference between W and ZB structures: in W we find *two* bond distances which differ in length by about 13% while in the ZB structure there is only *one* bond length. This is an intrinsic property of the binary constituents and persists in the alloys. Also, the small splitting of the first-neighbor cation–anion bonds in the W structure is preserved in the alloy, but obscured by the bond length broadening. The calculated cation–cation and anion–anion bond lengths are shown to exhibit almost identical values in the W and ZB structures. The cation–cation bonds exhibit three distinct values corre-

sponding to A–A, A–B, and B

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