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Ordered structures in III-Nitride ternary alloys

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ABSTRACT

An efficient evolutionary structure prediction algorithm in combination with *ab initio* calculations is implemented in order to reveal energetically favorable superstructures of the III-Nitride ternary alloys. Several $2 \times 2 \times 2$ 32-atom supercells are used to explore the full range of concentrations, from $x = 0$ to 1. The formation enthalpies, bandgaps, clustering and/or ordering of the atoms are investigated and the results are discussed.

The formation enthalpy plots show local minima at specific concentrations, namely for $x = 0.25$, 0.50 and 0.75, that correspond to ordered structures. The valance band maxima, conduction band minima, bandgaps and the composition-independent bowing parameters for 2nd order Vegard's equation are calculated. The bandgap deviations from 1st order Vegard's law show total maxima at specific concentrations. The formation enthalpies and the bandgaps cannot be accurately described by single composition-independent bowing parameters, but the bandgaps are sufficiently described by composition-dependent bowing parameters, that are established.

In order to verify the rationality of the results against the size of the *ab initio* supercells, molecular dynamics calculations of $14 \times 14 \times 14$ supercells of $\sim 10^4$ atoms using bond-order interatomic potentials are performed. The obtained local minima of the formation enthalpy for the specific alloy compositions concur with those predicted by *ab initio* calculations proving the results are not influenced by the supercell size.

1. Introduction

Nitride alloys have been recognized as materials of significant importance for optoelectronic devices [1]. Although various studies on wurtzite nitride alloys have been reported [i.e. 2–11], the effect of the metallic mixing (ordered-disordered structures) on the electronic and optical characteristics is still under investigation. There have been many theoretical studies for the bandgap dependence on the alloy concentrations [12–16], but the results are based on a large set of different structural configurations, disordered and ordered. The disordered structures can be described as randomly distributed metallic atoms in a supercell, while on the ordered structures the atoms occupy specific crystallographically defined sites in the lattice. In the experimentally observed cases disordered as well as ordered structural configurations may coexist in these alloys. However, in all the cases the arrangement of the metallic atoms in the structures is driven by the several growth parameters. In order to investigate the distribution of the metallic atoms in both the disordered and ordered structures, various computational approaches have been implemented [17–20] taking into account the required formation energy. Initially Northrup et al. [21], proposed a model in order to explain simple 1×1 ordering with alternating Ga and Al/In rich layers. Recently Xu et al. [5], concluded by the use of first principles calculations in seven low-energy order structural configurations for $2 \times 2 \times 1$ 16-atom $Ga_xAl_{1-x}N$ supercells. The concept of Special Quasirandom Structures (SQS) has also been employed [17]. The method generates structures by occupying all possible lattice sites in a given supercell and successfully provides optimal disordered states within the frame of a periodic supercell approximation. The exhaustive algorithms scale poorly with the number of atoms, limiting the method to small supercells. Gan et al. [15] used this method to calculate the thermodynamic properties of wurtzite and zinc-blende $In_xGa_{1-x}N$ alloys producing optimal, but still disordered, 32-atom structures for $x = 1/4$, 1/2 and 3/4. An alternative approach by de Carvalho et al. [16] uses the cluster expansion method [18,19], in which $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloy structures are divided into a number of clusters, which are grouped into classes according to lattice symmetry. The authors used 16-atom $2 \times 2 \times 1$ supercells and found more or less ordering along the main crystallographic directions. Atomic ordering has been identified also experimentally in $Ga_xAl_{1-x}N$ and

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Table 1
Lattice constants and bandgap values for AlN, GaN and InN calculated under LDA, GGA and HSE approaches.

		LDA	GGA	HSE	Experimental
AlN	a (Å)	3.091	3.128	3.104	3.111 [41]
	c (Å)	4.949	5.018	4.97	4.980 [41]
	E_g (eV)	4.4	4.06	5.63	6.20 [42]
GaN	a (Å)	3.156	3.215	3.183	3.189 [43]
	c (Å)	5.145	5.239	5.176	5.185 [43]
	E_g (eV)	2.12	1.73	3.27	3.50 [44]
InN	a (Å)	3.505	3.584	3.539	3.538 [45]
	c (Å)	5.672	5.786	5.711	5.703 [45]
	E_g (eV)	Negative	Negative	0.74	0.69 [46]

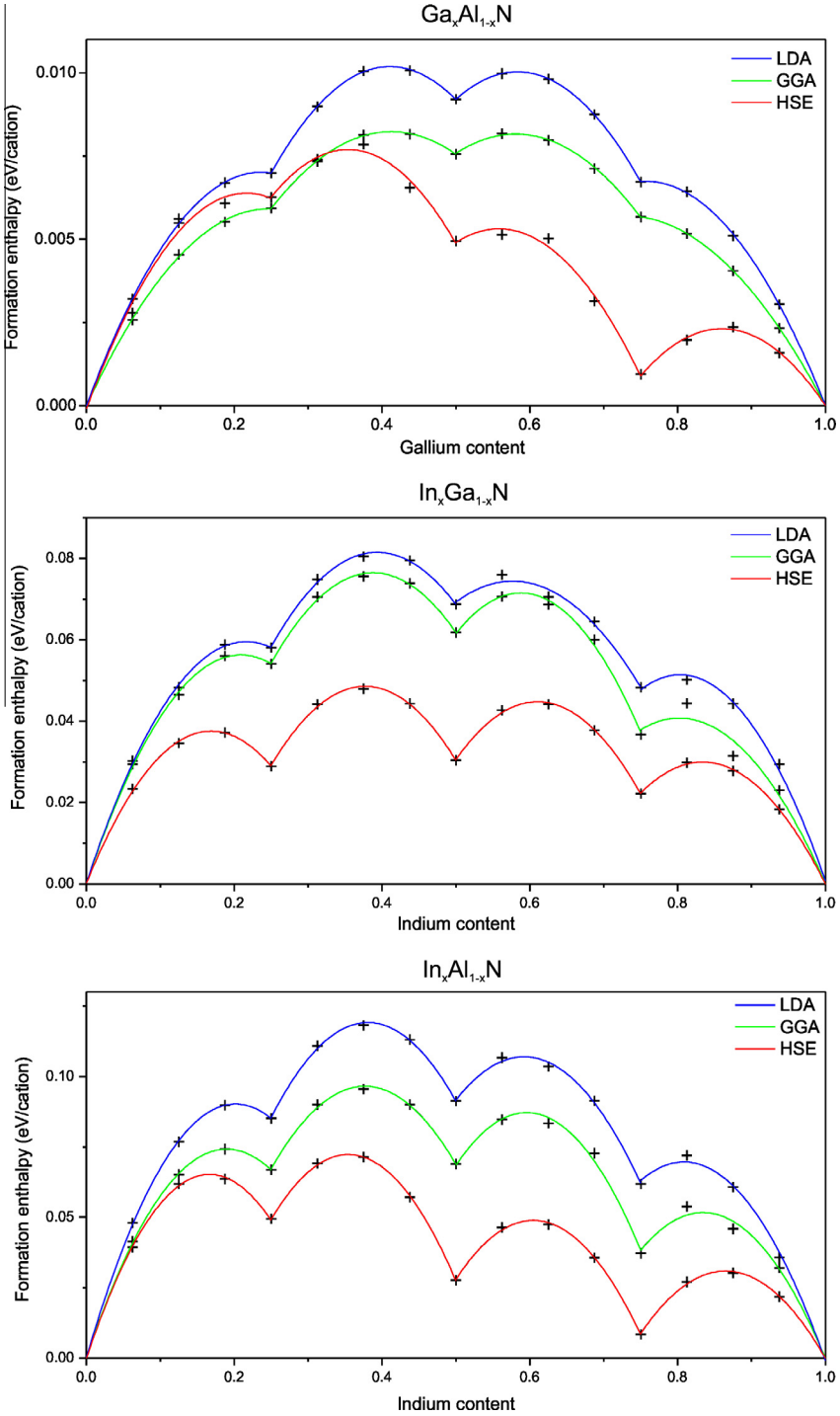

Fig. 1. Formation enthalpies per cation for the $Ga_xAl_{1-x}N$, $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ ternary alloys versus the metal content (Ga, In and In respectively) by the use of LDA, GGA and HSE.