Bonding and Energetics in Small Clusters of Gallium and Arsenic

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ABSTRACT: *Density functional theory is used to study the electronic, geometric, and bonding properties of small Ga_n, As_m, and Ga_nAs_m clusters with up to eight atoms. New ground state structures for many of these clusters are reported. Electronic states, stabilities, and charges are also reported and discussed in terms of the bonding in the clusters.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:189–196, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10127

INTRODUCTION

The III–V semiconductors are known for their uses in the microelectronics industry. Bulk properties are well studied; however, applications involving epitaxial growth and interactions at the interface of films and bulk material require an understanding of the semiconductors at the atomic level. Properties of new materials produced by the direct deposition of clusters of selected sizes may be cluster-dependent. We have recently explored the structures and properties of $(GaN)_n$ and $(AlN)_n$ clusters [1,2] using density functional theory (DFT) techniques. In this study, we expand the systematic investigation to Ga_nAs_m clusters, where $n + m \leq 8$.

Mixed clusters present a wealth of structural permutations and most previous studies on Ga_nAs_m clusters have been limited to either stoichiometric clusters, nonstoichiometric clusters of small sizes, or a small number of possible structures for larger nonstoichiometric clusters. The first computational study, by Lou et al. [3], used an LDA technique with numerical atomic orbitals to examine a selection of clusters of up to 10 atoms. Song et al. [4] subsequently used MP4 methods with the Hay-Wadt effective core potentials to calculate the structure of stoichiometric clusters of up to four monomer units. The smallest members of the Ga_nAs_m series were studied by Balasubramanian [5–7] using the CASSCF formalism, which appeared to overestimate the bond lengths and underestimate the binding energy. Most recently, Quek et al. [8] examined a range of structures with up to six atoms, using simulated annealing. Although this was a rather complete attempt at including all possible conformers, it appears that symmetric structures were given preference over more general forms, which were not reported in the study. Most recently, Piquini et al. [9] surveyed the same range of mixed clusters as reported here using perturbation theory to correct energies for electron correlation, after optimization using the Hartree–Fock approach. No geometric parameters were reported in that study, only the general structures.

Our results, using the B3PW91 functional with a frozen core approximation and triple zeta plus polarization basis sets for the valence electrons, show that As–As bonds dominate the structure for mixed clusters, often distorting an expected high-symmetry structure. After a brief description of the computational method, we discuss our results, beginning with the range of conformers examined and the observed ground state structures. We then discuss the

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bonding in the ground state clusters, their stability, and the effect of including relativistic corrections in the calculations.

COMPUTATIONAL METHODS

All of the reported calculations employed the Amsterdam Density Functional suite of programs (ADF 2.3.0) developed by Baerends, te Velde, and co-workers [10,11]. All atomic orbitals were represented by uncontracted triple-ζ STO basis sets with single polarization functions (Basis set IV within ADF). The gallium orbitals through 3d and the arsenic orbitals through 3p were assigned to the core and treated by the frozen core approximation [10]. In this approximation, the core orbitals are linear combinations of STOs and are selected so as to be orthogonal to the valence orbitals. The variational treatment of the wavefunction is applied only to the valence electrons after the valence basis set has been enlarged by the number of STOs in the core orbitals. The field due to the core is calculated in the first cycle, remains constant, and is used in all subsequent cycles. A set of auxiliary s, p, d, f, and g STO functions, centered on all nuclei, was used to fit the electron density and Coulomb and exchange potentials in the SCF cycles [12]. After comparison of a number of DFT methods (see Results), the Vosko–Wilk–Nusair [13] parameterization of the local density approximation was used along with gradient corrections to exchange as proposed by Becke [14] and to correlation as developed by Perdew et al. [15]. Geometry optimizations were carried out in the absence of symmetry constraints using the unrestricted formalism. These calculations will be referred to as B3PW91/TZP.

In the case of the relativistic results, core orbitals for both atoms are treated with a fully relativistic calculation to generate the frozen core potential. The subsequent calculation of the electronic structure is treated by means of a quasi-relativistic approach that includes the Darwin and mass–velocity corrections.

RESULTS AND DISCUSSION

Alternative DFT techniques were considered by using a simultaneous comparison of the calculated structures and binding energies for GaAs and As_2 with the available experimental values. The comparison is shown in Table 1. While there is little difference between the B3PW91 and B3P86 predictions of bond length or binding energy ($<1.5\%$ and $<3\%$ deviation, respectively) for the mixed dimer, the energy of the arsenic dimer is improved by the former functional and the B3PW91 method was chosen for the remainder of the study.

Bonding

Pure Arsenic or Gallium Clusters.   In any experiment producing mixed clusters, the probability of additional products via pure cluster formation is appreciable. For example, the production of GaAs films is accompanied by inclusion of As_2, which affects the film properties and, therefore, must be included in any computational modeling of the film. Similarly, we include the pure clusters in our study, both to check the computational method and as verification of accepted structures, if they are known. Ground state structures calculated for both As_n and Ga_n clusters are shown in Table 2. A wide range of structures was optimized for all of these clusters, including those of high symmetry and those with no symmetry at all. Many of the alternatives converged to the structures shown in the table. Those that did not had significantly smaller binding energies than the ground state structures in the table and are not included here.

The Ga_n structures obtained in this study are not all in agreement with previous computational work. Some deviation is simply a result of changes in bond lengths or bond angles, not in the gross structure. However, major differences in cluster geometry for some molecules are due to the previous studies being restricted to structures of high symmetry. The symmetric structures are not necessarily the minimum energy forms, since our results indicate that bonding configurations that avoid a gallium coordination number of 3 are more likely than other Ga_n structures.

The ground state of Ga_2 has been variously reported as $^3\Pi$ and $^3\Sigma_g^-$. Our calculations indicate that

TABLE 1   Comparison of Bond Lengths, r (Å), and Binding Energies, BE (eV), from DFT Methods Using the TZP Basis Set

	B3LYP [14,16]	PW91 [15]	B3PW91 [14,15]	B3P86 [14,17]	PW86/Perdew [17,18]	Experimental
GaAs	2.705	2.666	2.670	2.670	2.704	2.53 [19]
	2.01	2.11	2.03	2.06	2.13	2.06
As_2	2.138	2.122	2.122	2.121	–	2.103 [7,20]
	4.34	4.28	4.12	4.21	–	3.96

TABLE 2   Ground State Geometries for "Pure Clusters" of Arsenic or Gallium (Distances in Å)

Structure	$r_{X\text{-}X}$	Angle 1	Angle 2	Angle 3	BE (eV per Atom)	Notes
Ga_2	2.416	–	–	–	1.82 (0.91)	
Ga_3	2.661	60.00°	–	–	3.10 (1.03)	Equilateral triangle
Ga_4	2.720	90.00°	–	–	5.05 (1.26)	Square
Ga_5	2.618 2.797[a]	164.09°	95.69° ext.	84.50° opp. ext.	7.24 (1.45)	Substituted rhombus
As_2	2.122	–	–	–	4.05 (2.03)	
As_3	2.332 2.505[b]	65.00°	57.50° base	–	6.40 (2.13)	Isosceles triangle
As_4	2.460	60.00°	–	–	10.73 (2.68)	Tetrahedron
As_5	2.506 2.553[c]	90.00°	87.82° square to apex	–	11.85 (2.37)	Square pyramid

[a]To ext.
[b]Base.
[c]From apex.

the former is the ground state, lying 0.37 eV below the $^3\Sigma^-_g$ state that has a longer bond length (2.530 Å). The most recent dimer bond length has been reported [21], from DFT plus simulated annealing calculations, as 2.573 Å, whereas our value is 2.416 Å. However, it is clear that this difference is due to the difference in ground state assignment, since our excited state bond length is in good agreement with this earlier work. Previous reports of the trimer (equilateral triangle) geometry have resulted from the application of CASSCF-CI [22] and MRD-CI [23] methods. Our calculations indicate that the assignment [22] of the $^2A_1$ ground state of the trimer, rather than the quartet [23] spin state, is correct. This has been a contentious issue. Our bond lengths, 2.661 Å, however, are slightly elongated in comparison to those reported in Ref. [22]. The rhombic and square geometries of the tetramer, Ga_4, have been reported as nearly degenerate [23] from MRD-CI calculations. Tight binding molecular dynamics have indicated [8] that the rhombic form was lowest in energy with a relatively short bond length of 2.340 Å. Our calculations indicate that the ground state is square and that the bond lengths are longer, 2.720 Å, than those in the previous calculation. This longer bond length in Ga_4 is consistent with elongation of the bond length from the trimer. Finally, the current calculations indicate that the geometry of Ga_5 is not one of the symmetric forms previously reported. We have attempted to optimize a number of symmetric conformers, including that reported by Meier et al. [23]. However, we find that the ground state is a rhombic, nearly square, tetramer, with an additional external gallium atom. The bond lengths within the cyclic part of this cluster are slightly shortened over those of the tetramer (by approximately 2%), but are consistent in magnitude with those results. As shown below, this is consistent with the geometry of the gallium-rich Ga_4As cluster. The pentamer is a particularly clear example of the avoidance of three-coordinate gallium structures. The substituted rhombic structure is energetically preferred over the bicyclic pentamer form, even though the bond angle for the closed structure would not result in excessive strain. The existence of a ground state geometry of significantly lower symmetry than reported earlier has occurred for a number of other cluster systems and reflects the fact that constraint-free optimizations are now computationally less expensive and, hence, more feasible. In general for this assembly of clusters, the bond

lengths remain in the range from ~2.65 to ~2.70 Å and are substantially longer than the bond length in the dimer. The binding energy per atom is a monotonically increasing function of the cluster size.

Quek et al. [8] summarized the previous results for the arsenic dimer. The best agreement between theory and experiment was obtained for CCSD calculations using a double-ζ plus polarization basis set [24]. Our dimer bond length is within 1% of the experimental value [25], and hence in excellent agreement with the ab initio method. The As_3 trimer is predicted by our calculations to have an isosceles geometry. This result is surprising in light of the equilateral geometry of Ga_3 and the demonstrated energetic benefits of As—As bonds. No previous values of bond lengths have been reported for this cluster. The arsenic tetramer, As_4, is a regular tetrahedron. A previous SCF calculation [24] predicted a bond length of 2.417 Å in a cluster with tetrahedron geometry, but the tight binding MD [8] study predicted a rhombic geometry for this cluster. An experimental [26] verification of the geometry is available, which indicates that the tetramer is a regular tetrahedron with a bond length of 2.435 Å and our result, 2.460 Å, is in good agreement with that value. Finally, the As_5 pentamer is predicted from our calculations to have a square pyramidal geometry. No previous geometry has been reported for this cluster. The elongation of the As—As bond continues as the cluster size increases. The binding energy per atom for arsenic clusters generally (with a single exception) increases with cluster size. Arsenic clusters can take on geometries with a coordination number of 4 (as in the pentamer), and three-coordinate arsenic must be an energetically favorable condition, since the As_4 cluster is significantly more stable than would be expected based on a linear interpolation of the binding energy per atom for the other As_n clusters.

Gallium-Rich Clusters. The geometries of the ground state clusters are shown in Table 3. Previous studies have focused on arsenic-rich clusters; so there is little data available for comparison. The exception is a study of the qualitative geometry of mixed clusters that reports only the overall geometry/symmetry, but not bond lengths or bond angles [9]. In that work the structures were optimized using the HF/MIDI level of theory, and energies were then calculated, from those geometries, using the same basis set and the MP2 formalism. In the discussion that follows, the general structures of the clusters are in agreement with Ref. [9], but the bond lengths and bond angles were not presented in that study and no quantitative comparison may be made to that work. The Ga_2As cluster takes on a bent geometry with a bond angle of 101.09° and a bond length of 2.453 Å. This geometry is not an isosceles triangle since the Ga—Ga distance is greater than 3 Å. The bond angle and bond length are somewhat greater than those from tight binding [24] or the LDA model of DFT [3]. Moving to larger clusters, the tight binding model predicts a rhombus-like geometry of Ga_3As. Our calculations indicate that this conformer lies 0.2 eV above the ground state pyramidal isomer. The latter deviates 24° from planarity and the bond lengths, 2.560 Å, are extended by approximately 5% from those obtained for the Ga_2As cluster. The next largest cluster, Ga_4As, exhibits a geometry that may be seen as derivative of the previous two. This planar cluster consists of an isosceles triangle with the two additional gallium atoms attached externally to the arsenic atom. The bond angles and bond lengths are too large to consider this to be a planar, three-triangle structure, again an instance of the avoidance of three-coordinate gallium–gallium bonding. Finally, a symmetric cluster, most accurately described as an arsenic dimer capped on three

TABLE 3 Ground State Geometries for Clusters with Gallium as the Major Atom (Distances in Å)

Structure		r_{Ga-Ga}	r_{Ga-As}	r_{As-As}	Angle 1	Angle 2	Angle 3	BE (eV per Atom)	Notes
Ga_2As		–	2.453		–	101.09°	–	4.45 (1.48)	Bent
Ga_3As		–	2.560	–	115.36° Ga–As–Ga	–	–	7.21 (1.80)	Pyram., 24° from planar
Ga_4As		2.736 2.641[a]	2.730	–	60.00° apex	69.02° triangle-Ga	162.70° Ga–As–Ga	8.92 (1.78)	Sub equilateral
Ga_3As_2		–	2.795	2.487	63.15° Ga–As–Ga	52.70° As–Ga–As	–	9.74 (1.94)	Capped dimer

[a]Substituents.

sides by a gallium atom, is found to be the ground state for the Ga_3As_2 cluster. This structure is lower in energy than a monocyclic ring, a bicyclic ring, a planar structure, or a linear structure. The As—As bond is extended from that seen in the isolated dimer, as expected for a four-coordinate atom. The Ga—As bond length is also greater than is typical for this type of bond. In general, for Ga_nAs structures, no ground state structures with a coordination number of 3 for gallium were observed. Moreover, the structures that were found to be of lowest energy always included the maximum number of Ga—As bonds and the minimum number of Ga—Ga bonds. The Ga_3As_2 cluster continues this trend and, in addition, the lowest energy structure includes As—As bonding. The binding energy per atom for these complexes increases with cluster size.

Arsenic-Rich Clusters.   The geometries are shown in Table 4. Our structures are similar, in general form, to those reported in Ref. [9]. While some comparison data from other previous calculations do exist and the calculations are in agreement as to the general structure, we find that our results differ in the details of bond length and bond angle. For the smallest cluster, $GaAs_2$, most of the previous work [3,7,8,23] is in agreement as to the overall structure of the cluster; however, there is disagreement on the bond lengths. Our results are in best agreement with the CASSCF results [7], especially when the As—As bond length, 2.208 Å, is given significance. The Ga—As bond distance is exceptionally long. The triangular shape is almost, but not quite, an arsenic dimer plus an associated gallium atom. Both the tight binding model and our DFT results indicate that the $GaAs_3$ structure is a planar,

rhomboid-like geometry with an internal Ga—As bond. However, our DFT results predict a structure that may be readily characterized as an arsenic trimer-like core capped by a gallium atom. The bond angles in this cluster are greater than those in the smaller $GaAs_2$ cluster. The $GaAs_4$ geometry is predicted to be a nonplanar As_4 rhombus capped by a gallium atom, while the Ga_2As_3 cluster is calculated to have a trigonal bipyramidal ground state geometry. There are no previous quantitative reports of the former and only the general shape, i.e. trigonal bipyramidal, has been reported [3] for the latter. The driving force for lowest energy structures in the $GaAs_n$ clusters is to maximize the number of As—As bonds. This is satisfied by structures of regular and high symmetry, such as observed for $GaAs_4$ and Ga_2As_3. The binding energy per atom is an increasing function of cluster size.

Stoichiometric Clusters.   Structures and binding energies for $(GaAs)_n$, where $n = 1$–4, have been studied. Table 1 includes GaAs and the remaining clusters are presented in Fig. 1. Our DFT-derived bond length for GaAs is comparable to that obtained in the studies summarized in Ref. [8], but our overall structure/energy prediction appears to be a distinct improvement if the bond length ($\sim$6% deviation) and the binding energy ($<$1% deviation) are used simultaneously as the comparison criteria. The structure of the dimer, Ga_2As_2, is in agreement with several previous reports. This cluster takes on a rhombic geometry with an internal As—As bond. Our bond lengths and bond angles confirm the earlier results using correlated *ab initio techniques*, which do not agree very well with the tight binding studies. The HF/MIDI studies did not locate the internal bond

TABLE 4   Ground State Geometries for Clusters with Arsenic as the Major Atom (Distances in Å)

Structure		r_{Ga-As}	r_{As-As}	Angle 1	Angle 2	Angle 3	BE (eV per Atom)	Notes
$GaAs_2$		2.859	2.208	45.45° apex	67.28° base	–	5.67 (1.89)	Isosceles triangle
$GaAs_3$		2.696	2.342 2.681[a]	69.84° As—As—As	59.63° As—Ga—As	85.44° Ga—As—As	8.86 (2.22)	Capped As_3 56.4° from planarity
$GaAs_4$		2.658 2.467[a]	2.495	88.10° As—Ga—As	60.36° Ga—As—As	95.59° As—As—As	11.74 (2.35)	Capped As_4
Ga_2As_3		2.676	2.564	112.83° Ga—As—Ga	60.00° As—As—As	57.25° As—Ga—As	10.91 (2.18)	Trigonal bipyramid

[a]Diagonal distance.

Dimer binding energy = 8.16eV

Trimer binding energy = 13.61eV

Tetramer binding energy = 17.86eV
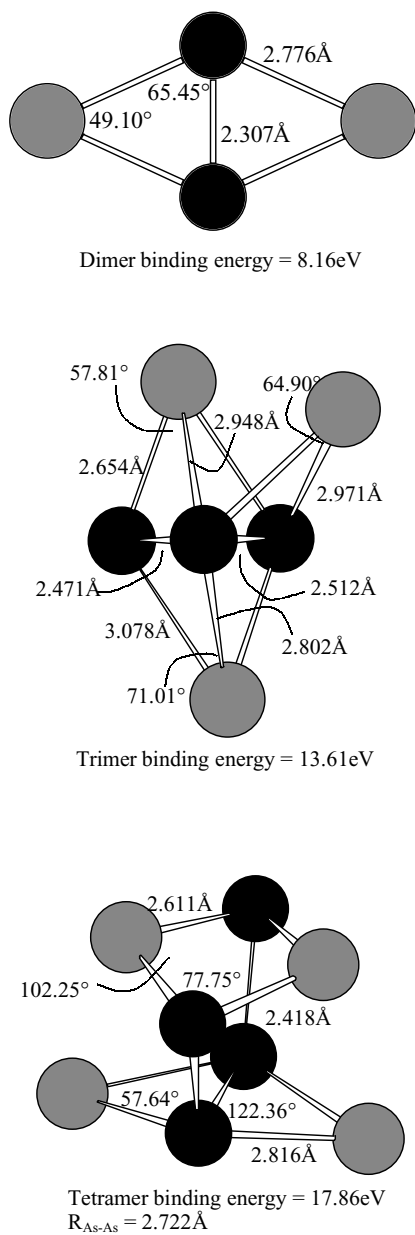R_{As-As} = 2.722Å

FIGURE 1   Structures and binding energies for the stoichiometric clusters with $n > 1$. The darker atoms are arsenic and the lighter atoms are gallium.

[9]. Two different structures have been reported for the trimer, Ga_3As_3, cluster. Lou et al. [3] report an edge-capped trigonal bipyramidal structure, while Song and co-workers [4], as well as Piquini et al. [9], report a Ga-capped As_3 triangle. Our structure (as shown in Fig. 1) is closer to that of the former, but is not identical. The ground state geometry does not include a symmetric trigonal bipyramidal core. The Ga—As bond lengths opposite the gallium cap are anomalous, one being elongated and one shortened. In addition, the As—As bond between the atoms

attached to the gallium cap is also elongated. Song et al. [4] reported a rhombic prism as the ground state conformer of the tetramer, Ga_4As_4. Earlier work [3] also reports that the cluster takes on a rhombic prism structure, but differs in that the prism includes an arsenic tetramer unit at its center. Contrary to our experience with other arsenic containing clusters, Ref. [9] reports a structure with a square Ga_4 as the core. Our results have a group of four arsenic atoms at the center; however, these atoms do not form an As_4 unit. Moreover, our structure, while three-dimensional, is not prismic. The dimensions of the upper and lower components are not identical. The binding energy per atom increases on moving from the dimer to the trimer, but no subsequent increase occurs upon increasing the cluster size to the tetramer.

Charges

Mulliken charges for a number of clusters are shown in Table 5. As expected, Ga is cationic and arsenic is anionic in all of the clusters. However, the charges (per atom) are relatively small and the bonding may be thought of as essentially covalent. Within the stoichiometric clusters, the charges are relatively constant and equal approximately 0.2e. This is substantially less than the 0.46e predicted using LCAO methods for bulk GaAs [4]. However, this difference may be a reflection of the fact that the cluster size examined in this study is too small to observe a trend toward the bulk value. As might be expected, non-stoichiometric clusters have charges that reflect the unique nature of the bonding within the cluster series. For example, the Ga charge increases with increasing fraction of As in the $GaAs_n$ series of clusters and similarly for the Ga_nAs clusters. The charge is dependent upon the number of bonds to the gallium or arsenic atom.

TABLE 5   Mullikan Charges for the Ground State Geometries of Mixed Clusters

Formula	q_{As}		q_{Ga}		
GaAs	−0.16		0.16		
Ga_2As	−0.42		0.21		
$GaAs_2$	−0.10		0.20		
Ga_2As_2	−0.18		0.18		
Ga_3As	−0.52		0.17		
$GaAs_3$	−0.17 (2)	−0.03	0.31		
Ga_4As	−0.41		0.15 (2)	0.05 (2)	
$GaAs_4$	−0.13 (2)	−0.02 (2)	0.31		
Ga_3As_2	−0.17	−0.14	0.15	0.11	0.06
$GaAs_3$	−0.20 (2)	−0.00	0.20 (2)		
Ga_3As_3	−0.19 (2)	−0.11	0.12 (2)	0.25	

Stability

The stability of the clusters was examined by calculating the binding energy per atom (presented in Tables 2–4 and Fig. 1) as well as the energetics of dissociation pathways (shown in Table 6). The binding energy per atom is defined as $E = \{nE_{Ga} + mE_{As} - E_{Ga_nAs_m}\}/(n + m)$. We consider the pure and mixed clusters separately.

As expected based upon dimer bond strengths, the binding energy per atom is greater for the As_n clusters than for the Ga_n molecules. For gallium, the energy rises monotonically with increasing cluster size, and fitting the cluster binding energies to a linear regression of E vs. $n^{-1/3}$ yields a prediction ($n = \infty$) of the bulk binding energy of 2.25 eV. This value should be compared to the experimental value of 2.979 eV. The arsenic cluster binding energy per atom also increases with cluster size; however, the As_4 cluster shows such exceptional stability that its value does not follow the pattern set by the other three clusters, which yield a bulk value of 3.36 eV, compared to an experimental value of 3.14 eV. Our small sample set is reflected in the deviation of

extrapolated values from the experimental results. For mixed clusters (Tables 3 and 4), we see that the binding energies fluctuate with cluster structure and no clear trend may be discerned, except to note that some particular cluster sizes are more stable than others, an expected result of unfavorable (or favorable) bonding situations within a particular cluster. This effect was also noted in earlier computational studies of nonstoichiometric clusters [3].

All of the clusters are stable with respect to fragmentation at normal temperatures. The smallest Ga_n clusters show a slight preference for dissociation into the dimer channel. The data indicate that arsenic cluster dissociation is more unfavorable than gallium cluster dissociation, but would preferentially occur in channels leading to the dimer or tetramer. The dissociation for mixed clusters follows the pattern expected from the discussion of the bonding in these molecules. Gallium-rich clusters prefer pathways that lead to mixed Ga—As products, while arsenic-rich clusters prefer pathways that provide As_n clusters. The dissociation of stoichiometric clusters is driven by the energetics of arsenic cluster formation. For example, the dissociation of tetramers

TABLE 6   Fragmentation Energies (in eV) Along Various Dissociation Pathways

$Ga_2As \rightarrow$	$GaAs + Ga$	2.42	$GaAs_2 \rightarrow$	$As_2 + Ga$	1.55
	$Ga_2 + As$	2.97		$2GaAs + As$	3.61
$Ga_3As \rightarrow$	$Ga_2As + Ga$	2.75	$GaAs_3 \rightarrow$	$As_3 + Ga$	2.46
	$Ga_2 + GaAs$	3.73		$As_2 + GaAs$	2.78
	$Ga_3 + As$	4.08		$GaAs_2 + As$	3.16
$Ga_4As \rightarrow$	$Ga_2 + Ga_2As$	3.02	$GaAs_4 \rightarrow$	$As_4 + Ga$	0.96
	$Ga_3 + GaAs$	3.79		$As_2 + As_2Ga$	2.00
	$Ga_4 + As$	3.84		$As_3 + GaAs$	3.29
$Ga_3As_2 \rightarrow$	$Ga_2As_2 + Ga$	1.58	$Ga_2As_3 \rightarrow$	$Ga_2As + As_2$	2.41
	$Ga_3As + As$	2.50		$GaAs_3 + Ga$	2.68
	$GaAs_2 + Ga_2$	2.62		$Ga_2As_2 + As$	2.72
	$Ga_3 + As_2$	2.62		$As_3 + Ga_2$	2.73
$Ga_2As_2 \rightarrow$	$Ga_2 + As_2$	2.08	$Ga_4As_4 \rightarrow$	$2Ga_2As_2$	1.54
	$2GaAs$	4.10		$Ga_4 + As_4$	2.08
	$2Ga + 2As$	8.09		$Ga_3As_3 + GaAs$	2.36
				$Ga_3As + GaAs_3$	2.43
$Ga_3As_3 \rightarrow$	$Ga_3As + As_2$	2.35		$Ga_2As_3 + Ga_2As$	2.50
	$Ga_2As_2 + GaAs$	3.42		$Ga_3 + GaAs_4$	3.54
	$GaAs_3 + Ga_2$	3.94		$4GaAs$	9.74
	$Ga_3 + As_3$	4.11			
	$3GaAs$	7.52			
$Ga_2 \rightarrow$	$2Ga$	1.81	$As_2 \rightarrow$	$2As$	3.99
$Ga_3 \rightarrow$	$Ga_2 + Ga$	1.29	$As_3 \rightarrow$	$As_2 + As$	2.38
$Ga_4 \rightarrow$	$2Ga_2$	1.41	$As_4 \rightarrow$	$2As_2$	1.63
	$Ga_3 + Ga$	1.94		$As_3 + As$	4.30
$Ga_5 \rightarrow$	$Ga_3 + Ga_2$	1.94	$As_5 \rightarrow$	$As_4 + As$	1.09
	$Ga_4 + Ga$	2.18		$As_3 + As_2$	1.45

to As_4 and Ga_4 is one of the lower energy pathways, as is the dissociation of the trimer to Ga_3As and As_2.

Relativistic Effects

The relativistic form of ADF was employed on the dimer structure, the stoichiometric mixed clusters, and the gallium-rich clusters. Results for the reference dimers are shown in Table 1. The dimer binding energies are decreased, providing slightly better agreement with the experimental values. However, the bond lengths, especially for the mixed dimer, increase and the agreement becomes less satisfactory. The differences among binding energies for any of the isomers of clusters larger than the dimer is sufficiently great, typically more than 0.5 eV, that the energy changes due to relativistic corrections do not alter the energy ordering of the conformers. The cluster with the smallest difference between conformers is Ga_4As (0.05 eV). In this instance, both the ground state structure shown in Table 3 and the conformer with the next lowest energy, the planar tricyclic form, are shifted to lower energies, the ground state more so than the higher energy form. Bond lengths in the mixed clusters tend to increase slightly with relativistic corrections. It appears that relativistic corrections are not necessary for the GaAs clusters studied here.

CONCLUSIONS

Density functional theory was used to study the electronic, geometric, and bonding properties of small Ga_n, As_m, and Ga_nAs_m clusters of up to eight atoms. New ground state structures for many of these clusters are reported and structures for clusters larger than the dimer are not necessarily in agreement with any previously reported results. The results have shown that mixed clusters form structures to maximize the number of gallium–arsenic or arsenic–arsenic bonds and minimize the number of gallium–gallium bonds. This energy minimization is the driving force that results in the asymmetric geometries of the ground state clusters. All of the clusters are thermodynamically stable, but the arsenic tetramer stands out as exceptionally stable. It is clear

that attempts to model molecular GaAs prepared on substrates must include the possibility of unintended mixed clusters as well as pure gallium and arsenic clusters in the films.

REFERENCES

[1] BelBruno, J. J. Chem Phys Lett 1999, 313, 795.
[2] BelBruno, J. J. Heteratom Chem 2000, 11, 281.
[3] Lou, L.; Wang, L.; Chibante, L. P. F.; Laaksonen, R. T.; Nordlander, P.; Smalley, R. E. J Chem Phys 1991, 94, 8015.
[4] Song, K. M.; Ray, A. K.; Khowash, P. K. J Phys B 1994, 27, 1637.
[5] Balasubramanian, K. Chem Phys Lett 1988, 150, 71.
[6] Balasubramanian, K. J Molec Spectrosc 1990, 139, 405.
[7] Balasubramanian, K. Chem Phys Lett 1990, 171, 58.
[8] Quek, H. K.; Feng, Y. P.; Ong, C. K. Z Phys D 1997, 42, 309.
[9] Piquini, P.; Canuto, S.; Fazzio, A. Nanostruct Mater 1998, 10, 635.
[10] Baerends, E. J.; Ellis, D. E.; Ros, P. Chem Phys 1971, 2, 41.
[11] te Velde, G.; Baerends, E. J. J Comput Phys 1992, 99, 84.
[12] Krijin, J.; Baerends, E. J. Fit Functions in the HFS Method; Free University of Amsterdam: The Netherlands, 1981.
[13] Vosko, H. S.; Wilk, L.; Nusair, N. Can J Phys 1980, 58, 1200.
[14] Becke, A. D. Phys Rev A 1988, 38, 2398.
[15] Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Phys Rev B 1992, 46, 6671.
[16] Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 37, 785.
[17] Perdew, J. P. Phys Rev B 1986, 33, 8822.
[18] Perdew, J. P.; Wang, Y. Phys Rev B 1986, 33, 8800.
[19] Lemire, G. W.; Bishea, G. A.; Heidecke, S. A.; Morse, M. D. J Chem Phys 1990, 92, 121.
[20] Balasubramian, K. J Mol Spectrosc 1987, 121, 465.
[21] Jones, R. O. J Chem Phys 1993, 99, 1194.
[22] Balasubramanian, K.; Feng, P. Y. Chem Phys Lett 1988, 146, 155.
[23] Meier, U.; Peyerimhoff, S. D.; Grein, F. Z Phys D 1990, 17, 209.
[24] Shen, M.; Schaefer, H. F., III. J Chem Phys 1994, 101, 2261.
[25] Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure IV; Van Nostrand Reinhold: New York, 1979.
[26] Morino, Y.; Ukaji, T.; Ito, T. Bull Chem Soc Jpn 1966, 39, 64.