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Theoretical study on structures of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters*

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The structures of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters are studied using the full-potential linear-muffin-tin-orbital molecular dynamics (FP-LMTO MD) method. Four structures for Ga_3N, five structures for GaN_3, nine structures for Ga_3N_2 and nine structures for Ga_2N_3 have been obtained. The most stable structures of these clusters are planar ones. A strong dominance of the N—N bond over the Ga—N and Ga—Ga bonds appears to control the structural skeletons, supporting the previous result obtained by Kandalam and co-workers. The most stable structures of these small GaN clusters displayed semiconductor-like properties through the calculation of the HOMO–LUMO gaps.

Keywords: FP-LMTO MD method, GaN clusters, geometrical and electronic structures
PACC: 3640, 6146, 3520D

1. Introduction

Atomic clusters represent a new phase of matter between molecules and solids, and show increasing potential for technological applications; as a result of this, their structures and energetics have been the focus of many experimental and theoretical studies in the past few years.[1–5] The structure and electronic properties of clusters can be dramatically different from those of the bulk due to the high surface area to volume ratio. The addition of a few atoms to a cluster can also result in a major structural rearrangement. With the rapid advances in science and technology, electronic devices have been reduced in size and the behaviour of semiconductor surface properties has thus gained much more attention. The relation between the geometry and the electronic structure plays a critical role in dictating the properties of a material. GaN is an important wide band-gap semiconductor, and has recently emerged as a material of choice for applications in the microelectronic and optical industry.[6] This has led to numerous theoretical and experimental studies on structural, electronic and optical properties of both surface and bulk phases of GaN. However, less attention has been paid to the research of GaN clusters, though the proposed application of GaN in microelectronic devices requires an understanding of the physical and chemical properties of the clusters on the atomic level. For example, in order to prepare electronic devices, GaN nanoclusters can be made by using sequential ion implantation in a dielectric matrix.[7] This may be viewed as nanoclusters of GaN adsorbed over the surface of a thin film.

For the study of GaN clusters, some theoretical calculations, which are concerned with small clusters of GaN, have been performed. A notable theoretical contribution came from Kandalam and co-workers.[8–11] Kandalam *et al* calculated the structures of Ga_nN_m (n,m=1, 2)[8] and Ga_nN_n (n=3–6)[9,10] clusters based on the nonlocal density approximation to the density functional theory. They suggested four structures for GaN_2, three structures for Ga_2N, five structures for Ga_2N_2, twelve structures for Ga_3N_3 and three structures for Ga_mN_m (m=4,5,6) clusters. They pointed out that N—N bonds play a crucial role in stabilizing the cluster, and the structures are dominated either by N_3 or N_2 subunits. Belbruno[12] investigated the structures of Ga_nN_n (n=2–4) clusters using density functional theory. Four structures for Ga_2N_2, three structures for Ga_3N_3 and three structures for Ga_4N_4 were investigated in his calculations. Costales and Pandey[13] calculated the structures of small Ga_nN_n (n=1–3) anionic clusters based

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on density functional calculations. However, none of these previous theoretical studies have considered Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters, to the best of our knowledge. Theoretical studies of larger mixed clusters have been comparatively limited due to the computational difficulties associated with the structural as well as permutational variations resulting from the presence of more than one elements.

In this paper, we carry out the calculations for small Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters using the full-potential linear-muffin-tin-orbital molecular dynamics (FP-LMTO MD) method. The accuracy of cluster version of this approach has been confirmed by our previous studies (for example, Refs.[14–19]) on small Si_n, P_n, B_n, Ge_n, Ga_nAs_n clusters. We report their structures and energies and discuss the electronic structures of the small GaN clusters.

2. Method

The FP-LMTO method [20,21] is a self-consistent implementation of density functional theory within the local-density approximation. Here we give just a brief description of the main features of the method. The real space is divided into two regions: the muffin-tin spheres, where the charge density is described by a spherical harmonic expansion, and the interstitial region, where the charge is expressed by a linear combination of Hankel envelope functions with negative energies ($-0.4, -1, -2$ Ry, in our case). The Hankel functions are solutions to the Helmholz equation for a point source of spherical waves. The full-charge density, which is fitted to these functions, is used to solve Poisson's equation in the whole space and to evaluate the matrix elements of the full-potential. The fitting is tabulated as a function of the distance between muffin-tin spheres of two atoms from zero up to infinity. The tabulated density is used in the evaluation of the Harris functional [22] and its derivatives relative to the atomic displacement are used in calculating the forces.[23] Geometry optimization is carried out by using the forces on the nuclei. To minimize the electronic energy function (Harris energy function), we use a dynamical simulated annealing technique in which friction term is used to cool off. Each calculation is considered to be converged when the maximum of the forces is less than 0.001(Ry/Bohr), and variation in total energy is less than 10^{-4} Ry. The details of how the molecular dynamics simulation can be performed are given in Refs.[23,24]. For having a sufficiently high probability of finding the global minimum energy (ground state) structure, the number of initial structures is as large as possible. In the present calculations, all sphere radii for Ga and N are taken to be 2.10 and 1.00 a.u., respectively. The LMTO basis sets include s, p, and d functions on all spheres. The exchange-correlation potential of Hedin–Lundqvist [25] is employed.

3. Results and discussion

All possible connectivities of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 are searched on the FP-LMTO MD levels. However, in some cases, the geometrical optimization of several different starting configurations is found to give the same geometrical parameters upon optimization. In Figs.1–3, we present their final geometrical structures. In Table 1, we list their structural parameters and binding energies for the three lowest-energy isomers. We calculate the binding energy of each cluster of Ga_xN_y, given by E_b=xE(Ga)+yE(N)-E(Ga_xN_y), where E(Ga), E(N) and E(Ga_xN_y) are the energies of an isolated Ga atom, a N atom and the Ga_xN_y cluster. To explain the relative stability of the various isomers of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters, we should bear in mind the binding energies of the bonds occurring in a given configuration. Because the bond energy decreases on going from N—N to Ga—N and Ga—Ga, it is expected that the skeletons of the stable isomers of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters are governed by the relative strengths of the bond energies, favouring, in this order, the appearance of N—N, Ga—N and Ga—Ga sequences.

For Ga_3N, as shown in Fig.1, we obtained four final calculated structures. These final structures are obtained from nine initial structures. In our results, the lowest-energy structure is an equilateral triangle in which a central N is bound to three Ga atoms (Fig.1(a)). The Ga—Ga bond length is 0.3315nm, while the Ga—N bond length is 0.1914nm. The Ga—N bond length is somewhat shorter than that in bulk stoichiometric GaN. In bulk stoichiometric GaN the Ga—N distance is 0.194nm.[26] It is noted that the number of Ga—N bonds of structure (a) is the largest among all Ga_3N clusters presented. This factor combined with the observation of structure (a) as a planar structure with a threefold coordination of N provides a glimpse of the chemistry of the N atom. We recall that N is trivalent and NH_3 is a very stable molecule although the geometry of NH_3 is three-dimensional. The reason why structure (a) is planar has to do with the fact that the N—Ga bond should be more po-

larized towards the N atom than in the case of the N—H, with the N accepting more charge. This means a larger s character in the N part of the N—Ga bond, which is achieved by an sp^2 hybridization instead of being achieved by the sp^3 hybridization. A similar structure was reported for Al_3N cluster [27,28] as the most stable structure. Structure (b) is a bent Ga—N—Ga—Ga chain. It lies 1.85eV above structure (a). Structure (c) is a linear Ga—N—Ga—Ga chain, and is 1.93eV higher in energy than structure (a). Structure (d) is the least stable among the four stable structures. It is shown from Figs.1(a)–(d) that the energy of the cluster decreases as the number of the Ga—N bond decreases.

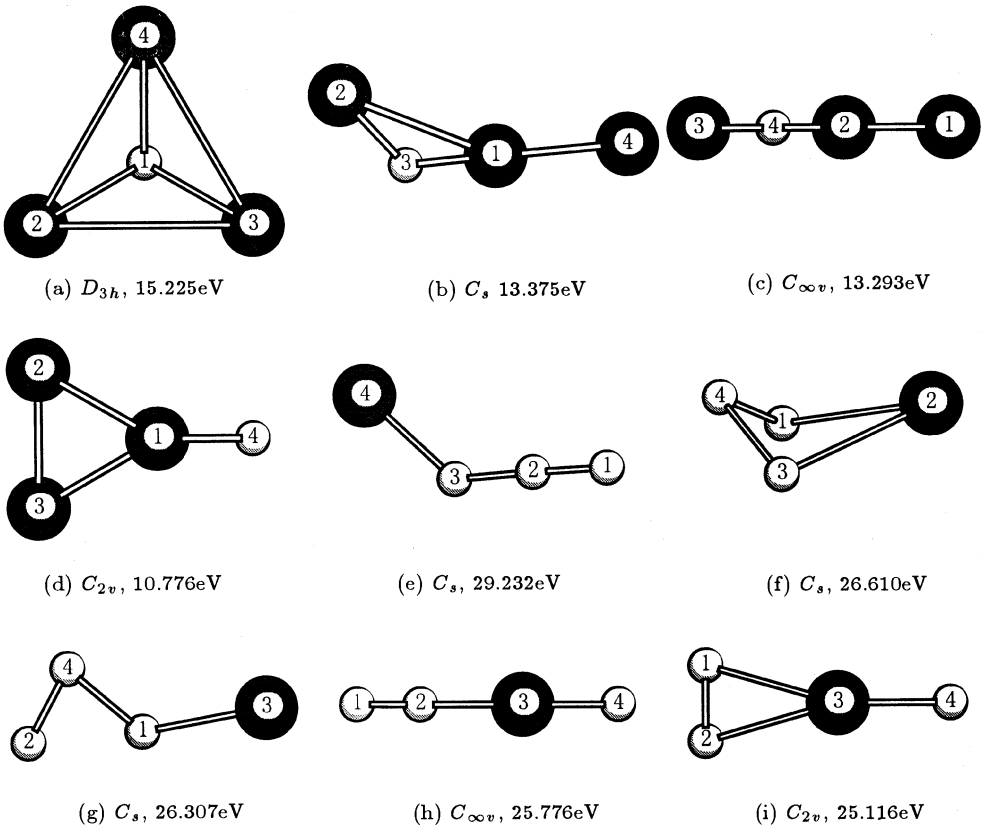


Fig.1. Geometries of the stable structures of Ga_3N and GaN_3 clusters, along with their symmetries and binding energies. Small circles represent N atoms, and large circles represent Ga atoms.

For GaN_3, we obtained five stable structures from relaxing ten initial structures. Structure (e) is the global lowest-energy isomer among these final structures. This structure is a bent Ga—N—N—N chain. The calculated bond lengths are 0.1881nm (Ga—N), 0.1211 (N(2)—N(3)) and 0.1145 (N(1)—N(2))nm, respectively. The Ga—N distance of the structure is shorter than that of bulk GaN_3. The N—N distances are quite close to those of the linear N_3 ion (i.e., 0.1185nm we obtained). Thus, the N—N bonds slightly deviate from the conventional covalent bond. The most stable structure for AlN_3 cluster is a linear Al—N—N—N chain.[27] We have also optimized this geometry for the GaN_3 cluster, and then obtained a bent Ga—N—N—N chain as shown in Fig.1(e). Structure (g) is a bent Ga—N—N—N chain too. This structure is found to be 2.925eV higher in energy than structure (e). We think that this energy difference is due to the bending of the N_3 unit, which breaks the double bonds that give N_3-ion its stability. Structure (f) is a three-dimensional (3D) structure with C_s symmetry, and is found to be 2.622eV higher in energy than structure (e). The calculated results for GaN_3 show that the isomers with N_3 subunit are preferred. This preference may results from much stronger N—N bonding than Ga—N bonding. In the previous study on Ga_nN_n clusters,[9,10] isomers containing N_3 subunit were also found to have lowest energies.

Table 1. Point groups, bond lengths and binding energies E_b for the three lowest energy structures of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters.

Species	Structure(point group)	Bond name	Bond length/nm	Binding energy/eV
Ga_3N	Fig.1(a) (D_{3h})	d_{12}	0.1914	15.225
		d_{24}	0.3315	
	Fig.1(b) (C_s)	d_{13}	0.1773	13.375
		d_{12}	0.3267	
		d_{14}	0.2593	
		d_{23}	0.1869	
	Fig.1(c) ($C_{\infty v}$)	d_{12}	0.2595	13.293
		d_{24}	0.1764	
		d_{34}	0.1862	
GaN_3	Fig.1(e) (C_s)	d_{12}	0.1145	29.232
		d_{23}	0.1211	
		d_{34}	0.1881	
	Fig.1(f) (C_s)	d_{12}	0.2063	26.610
		d_{14}	0.1311	
	Fig.1(g) (C_s)	d_{24}	0.1213	26.307
		d_{14}	0.1410	
		d_{13}	0.1839	
Ga_3N_2	Fig.2a (C_{2v})	d_{12}	0.3051	22.926
		d_{14}	0.1922	
		d_{24}	0.2158	
		d_{45}	0.1255	
	Fig.2(b) (C_s)	d_{12}	0.2159	22.776
		d_{13}	0.3172	
		d_{15}	0.2054	
		d_{25}	0.1320	
		d_{23}	0.1923	
	Fig.2(c) (C_1)	d_{12}	0.2352	22.776
		d_{15}	0.2173	
		d_{14}	0.2609	
		d_{24}	0.2312	
		d_{25}	0.1197	
		d_{23}	0.2009	
		d_{34}	0.2523	
Ga_2N_3	Fig.3(a) (C_{2v})	d_{12}	0.1143	30.096
		d_{13}	0.1221	
		d_{34}	0.2042	
		d_{45}	0.2737	
	Fig.3(b) (C_{2v})	d_{14}	0.1187	29.699
		d_{15}	0.2101	
		d_{25}	0.3147	
	Fig.3(c) (C_s)	d_{13}	0.1210	29.531
		d_{12}	0.2337	
		d_{14}	0.1349	
		d_{23}	0.2171	
		d_{24}	0.2029	
		d_{45}	0.1891	

For Ga_3N_2, we tried 26 initial structures and finally nine structures were obtained. These structures are shown in Fig.2. Structures (b) and (c) are 3D structures, while the others are planar structures. Sectorial structure (a) is the lowest-energy structure among these nine structures. The bond lengths of the structure lie from 0.1255 (N—N) to 0.3051 (Ga—Ga)nm. In this structure there are four Ga—N bonds and one N—N bond. The bond lengths (0.1922nm) of Ga(1)—N(4) and Ga(3)—N(5) are somewhat smaller than that in stoichiometric GaN. The N—N bond of this structure is slightly elongated from the N_2 dimer bond length of 0.1102nm obtained by us. In this configuration, the N—N bond length is indicative of a double bond. Compared with other isomers presented in Fig.2, it is found that the multiple character of the N—N bond would further reduce by increasing the number of the coordination of N_2 (see Table 1). This result is in agreement with the previously reported result.[11] Structure (b) is degenerate with structure (c). They lie 0.15eV above the structure (a). The binding energies of structures (d) and (e) are very close. They are 0.22eV higher in energy than structure (a). Structures (f), (g), (h) and (i) are 0.42, 0.82, 1.27 and 1.50eV higher in energy than structure (a), respectively. In this case, the calculated results show that the isomers with N_2 subunit are preferred. This can be explained in terms of the N—N bond. In the previous study on Ga_2N_2 clusters,[8,12] the isomer containing N—N bond was also found to have lowest energy.

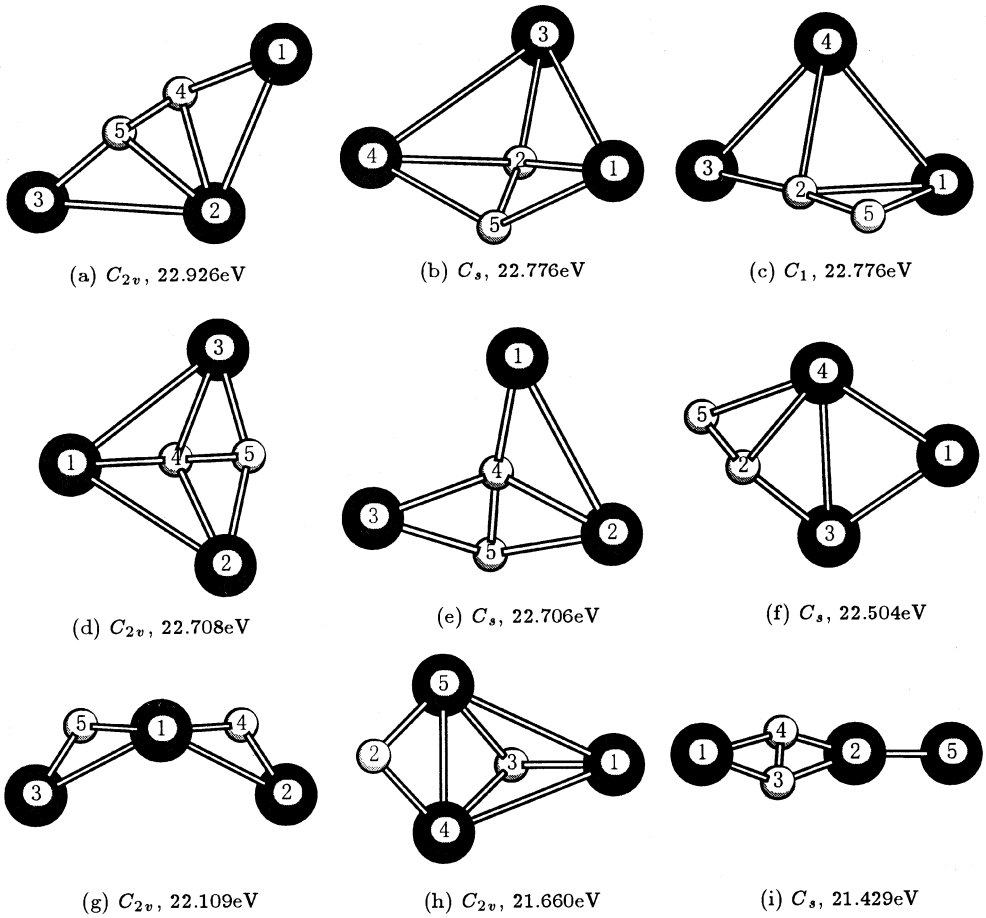


Fig.2. Geometries of the nine stable structures of Ga_3N_2 clusters, along with their symmetries and binding energies. Small circles represent N atoms, and large circles represent Ga atoms.

For Ga_2N_3, we tried 25 initial structures and finally also nine structures were obtained. The structures are shown in Fig.3. Structures (f) and (g) are 3D structures, while the others are planar structures. Structure (a) is the lowest-energy structure among nine final structures. This structure is a planar C_{2v} structure with bond lengths from 0.1143 (N—N) to 0.2737 (Ga—Ga)nm. It can be obtained from

GaN_3 isomer (see structure (e) in Fig.1) by adding another Ga atom. In this structure the Ga—N distances (0.2042nm) are a little larger than the corresponding distance in bulk GaN. However, the N(2)—N(1)—N(3) distances slightly deviate from that of N_3 ion. Planar structure (b) lies 0.40eV above the structure (a). This energy difference comes from the larger Ga—N and Ga—Ga distances in structure (b) than in structure (a). Planar structure (c) lies 0.57eV above the structure (a). The binding energy of structure (d) is almost the same as that of structure (c). Structure (d) is a bent Ga—Ga—N—N—N chain. Structure (e) is found to be 0.62eV higher in energy than the structure (a). Structures (f), (g), (h) and (i) are found to be 1.54, 2.14, 4.00 and 6.98eV higher in energy than structure (a). This is similar to the case of GaN_3; the calculated results for Ga_2N_3 show that the isomers with N_3 subunit are preferred.

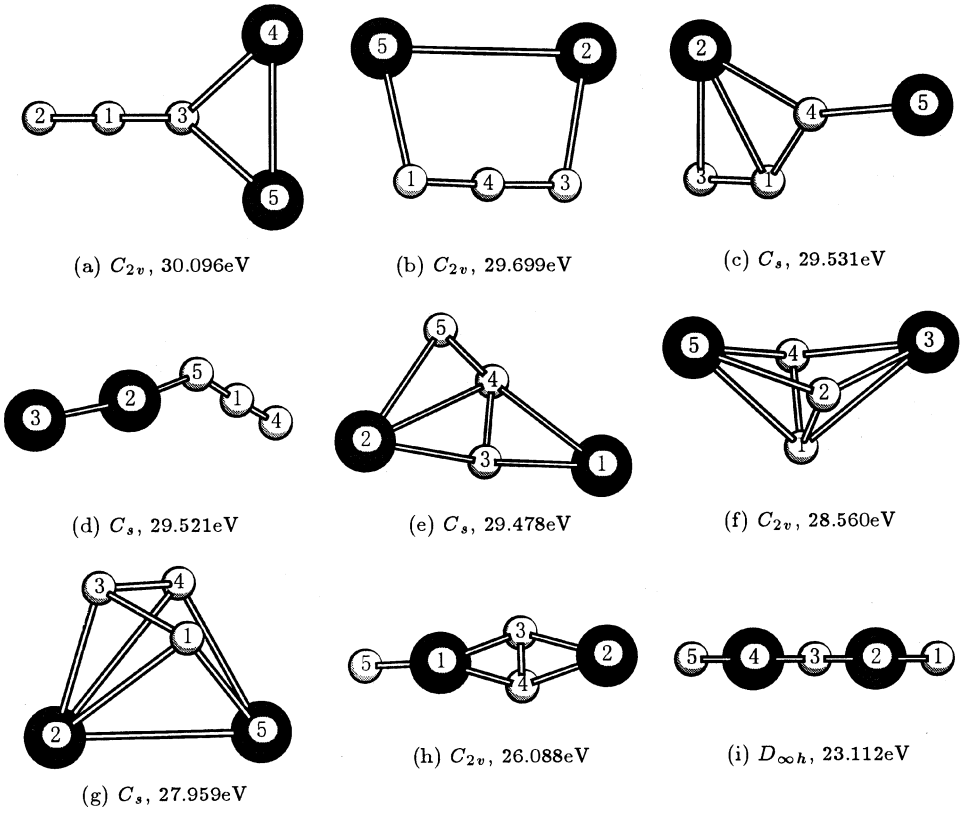


Fig.3. Geometries of the nine stable structures of Ga_2N_3 clusters, along with their symmetries and binding energies. Small circles represent N atoms, and large circles represent Ga atoms.

Table 2. Fragmentation energies for the most stable structure of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters.

Reaction	Energy/eV
$Ga_3N \rightarrow N+Ga_3$	11.959
$Ga_3N \rightarrow Ga_2N+Ga$	4.308
$Ga_3N \rightarrow GaN+Ga_2$	8.383
$GaN_3 \rightarrow N_3+Ga$	3.813
$Ga_3N_2 \rightarrow Ga_3+N_2$	0.148
$Ga_3N_2 \rightarrow Ga_2N_2+Ga$	2.010
$Ga_3N_2 \rightarrow GaN_2+Ga_2$	3.952
$Ga_2N_3 \rightarrow GaN_3+Ga$	0.865
$Ga_2N_3 \rightarrow N_3+Ga_2$	3.445

We now present the results on the relative stability of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters with respect to their fragmentation in atoms and clusters. We will only consider the lowest-energy configuration for each of the clusters involved, neglecting the contributions from the zero-point vibration energy. Table 2 is a collection of the fragmentation energies of the polyatomic nitride clusters dissociating via several possible paths. It is noteworthy that all of the fragmentation reactions are endothermic; that is, all of these clusters are stable with respect to their fragmentation into atoms and clusters. It can be found that fragmentation into atoms and small clusters is diffi-

cult for Ga_3N and GaN_3 clusters (around 4eV). However, considering the fragmentation paths, $Ga_3N_2 \rightarrow Ga_3+N_2$ and $Ga_2N_3 \rightarrow GaN_3+Ga$, the fragmentation energies are small. Thus, these fragmentation paths appear to be the preferred fragmentation paths for Ga_3N_2 and Ga_2N_3 clusters, respectively.

From the above structural description of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters, it is found that the structure of these clusters can be explained by the relative strengths of the bond energies. A strong dominance of the N—N bond over the Ga—N and Ga—Ga bonds appears to control the structures in this study. For Ga_3N_2, the isomer with a N_2 subunit is preferred. In the case of GaN_3 and Ga_2N_3, the isomer with a N_3 subunit is preferred. The present study supports the previous result obtained by Kandalam and co-workers.[8−10]

Table 3. Energy separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the lowest energy structures of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters.

Species	Structure (point group)	Energy separation/eV
Ga_3N	Fig.1(a) (D_{3h})	2.99
GaN_3	Fig.1(e) (C_s)	3.72
Ga_3N_2	Fig.2(a) (C_{2v})	1.43
Ga_2N_3	Fig.3(a) (C_{2v})	0.32
GaN crystal		3.44

Regarding the electronic structure of these clusters, we have focused on the HOMO–LUMO energy separation, which can be very important in the study of semiconductor materials. It can be considered that the HOMO–LUMO gap is equivalent to the energy gap in a bulk semiconductor. In Table 3, we present the HOMO–LUMO gap for the lowest-energy isomer of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters, including the values of the band gap of the wurtzite solid GaN[26] for the sake of comparison. Table 3 shows that the HOMO–LUMO gaps of these clusters are quite different, and the magnitude of the gaps changes from 0.32 to 2.99eV. Hence, these clusters may still exhibit semiconductor-like properties. The HOMO–LUMO gaps for Ga_3N and GaN_3 clusters are larger than those for Ga_3N_2 and Ga_2N_3 clusters. This may be explained by the closed shell in the case of Ga_3N and GaN_3. Comparing the respective band gap in solid GaN, we find that Ga_3N has a larger gap and the other clusters have smaller gaps.

4. Conclusions

Using the FP-LMTO MD method, we have carried out calculations for the structures of Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters. In this paper we have presented the structural results for these clusters theoretically. All the possible connectivities have been taken into consideration on the FP-LMTO level. In the case of Ga_3N and GaN_3, four and five structures have been obtained respectively. The most stable structure of Ga_3N is found to be an equilateral triangle in which a central N is bound to three Ga atoms. The ground state of GaN_3 is found to be a bent Ga—N—N—N chain. For Ga_3N_2 and Ga_2N_3, nine structures have been obtained. The most stable structure of Ga_3N_2 and Ga_2N_3 are found to have C_{2v} symmetry. A strong dominance of the N—N bond over the Ga—N and Ga—Ga bonds appears to control the structures in this study. This can be explained by the relative strengths of the bond energies. The present results support the results of Kandalam and co-workers.

The Ga_3N, GaN_3, Ga_3N_2 and Ga_2N_3 clusters are found to be stable against dissociation. The most stable structure of these small GaN clusters shows semiconductor-like properties through the calculation of the HOMO–LUMO gaps.

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