

Geometrical and electronic properties of Ga_nN_2 ($n = 1\text{--}18$) clusters: A density-functional investigation

Bin Song^{*}, Pei-Lin Cao

Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

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Abstract

The geometrical and electronic properties of Ga_nN_2 ($n = 1\text{--}18$) clusters have been investigated using the density functional theory within the generalized gradient approximation. The lowest-energy structures of these clusters have been obtained, and the trends in the geometries are discussed. The results show that the two N atoms prefer a peripheral position with a bulklike coordination as the cluster size increases. The two N atoms have the same coordination of Ga atoms in the most cases. It suggests that N atoms may distribute on the surface with similar bulklike coordination for large Ga-rich clusters with more N atoms. The Ga_nN_2 clusters at $n = 4, 6, 8, 10$ and 16 are found to possess relatively higher stability. The size-dependence of cluster properties such as binding energy, HOMO–LUMO gap, ionization potential, electron affinity, Mulliken charge and Ga–N bond length has been computed and analyzed. The bonding characteristics of the Ga_nN_2 clusters are discussed.

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1. Introduction

Atomic clusters containing a few to several hundreds of atoms consist of an intermediate regime between individual atoms and bulk solids [1]. In this regime, clusters bridge the gap between small molecule and bulk materials. Compared with bulk and film, clusters are expected to possess unique properties due to its special geometries and the quantum confinement effects. Gallium-nitride (GaN) is a very important wide band-gap semiconductor, and is gathering much attention from both the theoretical and experimental fields. The main reason behind this is its growing importance in the preparation of electronic devices [2]. Considerable progress has been made in the understanding of the structural, electronic and optical properties of both surface and bulk phases of GaN. However, unlike GaN crystal and film, the number of experimental and theoretical studies of GaN clusters is still lacking up to now. With the rapid advancement in science and technology, the size of the elec-

tronic devices is being reduced. A detailed knowledge of the geometrical and electronic properties of the GaN clusters could be specially valuable for understanding the growth mechanism of GaN-based materials and the use of low-dimensional GaN nanostructures in nanoscale materials and devices.

There have been several experimental studies concerning GaN clusters. Zhou and Andrews [3] have studied the reactions of laser-ablated gallium atoms with nitrogen atoms and molecules. Himmel and Hebben [4] have performed matrix-isolation experiments to study the interaction between Ga atoms and N_2 by using Raman and UV/Vis spectroscopies for detection and analysis. Very recently, Sheehan et al. [5] have presented the spectroscopic characterization of the ground and low-lying electronic states of Ga_2N via anion photoelectron spectroscopy. On the theoretical front, some research works have been reported with particular emphasis on the stoichiometric clusters (Ga_nN_n , $n = 1\text{--}12$) [6–15]. However, less attention has been paid to nonstoichiometric clusters. Kandalam et al. [6] and Costales et al. [16], calculated the structures, vibrational frequencies, energetics, and chemical bonding of Ga_2N and GaN_2 clusters using the nonlocal-density approximation to the density-functional theory (DFT). Wang and Balasubramanian

^{*} Corresponding author.

E-mail address: bsong@css.zju.edu.cn (B. Song).

[17] calculated the low-lying electronic states of Ga_2N , GaN_2 and the corresponding anions and cations. Our research group has reported the structures of Ga_nN_m ($n + m = 3-8$) clusters [18] by using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method based on DFT. We found that the structures, binding energies and HOMO–LUMO gaps of these clusters strongly depend on their size and composition. Recently, in order to understanding the equilibrium geometries and electronic structure of larger nonstoichiometric GaN clusters, we have taken a Ga_nN system as a test, and have performed theoretical investigation up to twenty atoms using the DFT within the generalized gradient approximation (GGA) [19]. It is found that the stable larger Ga_nN cluster may exist, and the N atom prefers peripheral position with a bulklike coordination. The results also indicate that the calculated energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the vertical ionization potential and the vertical electron affinity form an even–odd alternating pattern with increasing cluster size.

In the present Letter, we focus on nonstoichiometric Ga_nN_2 ($n = 1-18$) system. We report their size-dependent properties, including geometric structures, stabilities, bonding energies, ionization potentials, and electron affinities. This study is expected to provide further insight on the properties of Ga-rich GaN clusters, on one hand, and also to shed some light into the structure of large Ga-rich GaN clusters as the increase of N atoms in the cluster. The present study suggests that the N atoms may prefer a peripheral position with a bulklike coordination in large Ga-rich clusters, means that in large Ga-rich GaN clusters with more N atoms, stable Ga clusters may serve as the core, and the N atoms may distribute on the surface of the core Ga atoms.

2. Methods

All electron calculations were performed on Ga_nN_2 ($n = 1-18$) clusters, in the framework of DFT, using the DMOL³ program (Accelrys Inc.) [20]. The generalized gradient approximation using Perdew–Burke–Ernzerhof's (PBE) exchange–correlation functional was employed [21]. Double numeric basis sets, supplemented with d polarization functions (i.e., the DNP set) were used for all atoms in the cluster. The accuracy of the DNP basis sets has been confirmed by previous studies [6–8] on the group III-nitride clusters. Since some experimental results are available for the Ga and N atoms [22], we tested our theoretical results using various forms of exchange–correlation functionals, such as BP [23,24], PBE [21] and BLYP [24,25], using a DNP basis set in the DMOL³ program. Best results were obtained with PBE (Table 1). Thus, we have opted to use PBE functional for all Ga_nN_2 clusters. For accurate calculations, we chose an octupole scheme for the multipolar fitting procedure (the maximum angular momentum of the fitting function was set to be 3) on the charge density and Coulomb potential, and a fine grid scheme for numerical integration (about 1500 integration points per atom). Self-consistent field procedures were done with a convergence criterion of 10^{-6} a.u. on the energy and electron density. The geometric parameters were fully opti-

Table 1
Ionization potentials (eV) and electron affinities (eV) of Ga and N atoms

Method	Atom	IP	EA
GGA/DNP	Ga	5.79	0.39
Experiment [22]	Ga	5.99	0.30
GGA/DNP	N	14.85	1.31
Experiment [22]	N	14.53	–

mized without symmetry constraints. We used a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-5} a.u. on the total energy in the geometry optimization. All the calculations were carried out allowing for spin polarization. It is to be noted here that calculations were not performed for each spin state of the given cluster but the Aufbau principle as implemented in the DMOL³ program was used to obtain the optimal spin state of the cluster.

For each specific cluster size, an exhaustive search for minimum energy structures was performed by using a combination of FP-LMTO-MD [26–28] search and GGA minimization. The accuracy of the FP-LMTO-MD method for investigating the cluster structures has been confirmed by previous studies (for example, [14,18,29–31]) on small Si_n , Ga_nN_n , Ge_n clusters, etc. In order to perform the systematic search for the equilibrium structures of Ga_nN_2 ($n = 1-18$) clusters, we firstly used FP-LMTO-MD method to calculate the structures and energies in a global wide search. Large numbers of initial geometric configurations as seeds were relaxed until the local minimum of the total energy was found. For small Ga_nN_2 (n up to 2) clusters, all possible connectivities have been used as seeds. For larger Ga_nN_2 , the main initial atomic configurations were set up by random selections of atomic positions in three-dimensional space. The separation of Ga–Ga, Ga–N and N–N atoms was confined in a range. The range for Ga–Ga, Ga–N and N–N was 2.51–3.32 Å, 1.76–2.40 Å and 1.16–1.44 Å, respectively. The separation of any pair of atoms was set randomly when the seed structures were carried out. Depending on the cluster size, we selected 50–150 initial geometry configurations for geometry optimization. Then, the low-lying energy structures for each cluster size obtained by FP-LMTO-MD calculations were further optimized by using DMOL³ with GGA. No significant rearrangement occurred during the DMOL³ optimization process. In addition, we considered several other structures, which were generated by adding an N atom to the corresponding Ga_nN clusters [19], as our starting structures for straightforward geometry optimization. We also considered several other structures, usually with high symmetry, as our starting structures for straightforward geometry optimization. To make sure that the obtained lowest-energy structures are real local minima, normal-mode vibrational analyses were applied. All of the energy minima obtained for the most stable Ga_nN_2 clusters had no imaginary frequencies.

3. Results and discussion

3.1. Lowest-energy structures

The calculated lowest-energy structures for Ga_nN_2 ($n =$

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