

Quantum confinement effects in Gallium Nitride nanostructures: *Ab initio* investigations

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Abstract. We present *ab initio* density functional investigations of the atomic and electronic structure of gallium nitride nanodots and nanowires. With increasing diameter, the average Ga-N bond length in the nanostructures increases, as does the relative stability (heat of formation), approaching the values for bulk GaN. As the diameter decreases, the band gap increases, with the variation of the nanodots greater than that of the nanowires, in qualitative accordance with expectations based on simple geometrical quantum confinement considerations.

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1. Introduction

Semiconductor quantum dots have attracted large interest from the scientific community due to the unique quantum confinement effects and the resulting potential for size-tunable nanodevices.[1] Semiconductor quantum structures are expected to be used in future applications such as single-electron transistors, lasers and tunnelling diodes.[2] Gallium nitride (GaN) is a widely used III-V semiconductor in micro- and optoelectronic devices, such as blue light-emitting diodes and lasers. GaN quantum structures (or nanodots) have received particular attention for potential applications in light-emitting diodes[3, 4, 5] and high-temperature electronic devices.[2] GaN nanodots have been synthesised experimentally by various methods, including colloidal dispersion,[6] ion implantation,[7, 4] molecular beam epitaxy,[5] and metal-organic chemical vapour deposition.[8]

One of the most notable aspects of quantum confinement in semiconductors is the nanostructure size dependence of the band gap; namely, the band gap increases as the size decreases.[9, 10, 11] Using a simple effective-mass approximation particle-in-a-box model (EMA-PIB) for confinement in planar wells, cylindrical wires, and spherical dots, the band gap compared to the bulk value depends linearly on $1/d^2$ (where d is the diameter or thickness).[12] Such a simple description should be regarded as providing only a first approximation of quantum confinement in semiconductors; as the relevant dimension(s) of the nanostructure becomes very small this relationship can be expected to break down. It is however useful for showing how quantum confinement should depend on the geometry of confinement.

Theoretical investigations of GaN nanodots have used a range of computational methods including $k\cdot p$ theory,[13, 14] empirical forcefields,[15] tight-binding[16, 17] and density functional theory.[18] Many of these investigations use approximate or semi-empirical methods, and investigate the properties GaN nanodots mixed with other III-V nitrides. Calculations using $k\cdot p$ methods have typically examined GaN nanodots combined with e.g. AlN or InN, to investigate properties such as strain effects or exciton behaviour.[13, 14] Classical molecular dynamics has been used to investigate the thermal conductivity of GaN quantum dots coated with AlN.[15] Semi-empirical tight-binding calculations have been used to study optical transitions in InGaN-GaN quantum dots[16] and the affect of Mg doping in GaN nanodots.[17] An *ab initio* description of GaN nanodots will provide the most accurate description of the electronic structure, however there has been very few *ab initio* investigations. Li and Wang[18] have used a charge patching density functional method combined with band structure corrections (to yield the experimental effective masses) to a range of II-VI and III-V nitrides, including GaN quantum dots and wires. In particular they examined the ratios between the quantum confinement of dots and wires for particular materials, and mostly found good agreement with predictions using simple effective mass considerations.

We investigate the electronic structure of GaN nanodots using *ab initio* density functional theory (DFT) calculations. We examine how the atomic and electronic

structure (in particular the band gap and formation energy) of the nanodots vary as a function of the nanodot diameter, and compare this to results for GaN nanowires.

2. Methodology

Density functional theory calculations are performed using the DMol³ code[19, 20] where we employ the generalised gradient approximation (GGA) of Perdew, Burke and Ernzerhof.[21] The core electrons are represented by the semi-local DSPP pseudopotential,[22] with the valence electron configurations of gallium $3d^{10}, 4s^2, 4p^1$, and nitrogen $1s^2, 2s^2, 2p^3$. A double numerical basis set with polarisation functions is used for all atoms, with a real space cutoff of 9 Bohr. We generate GaN nanodots using our previously reported wurtzite bulk GaN ($a=3.18 \text{ \AA}, c=5.18 \text{ \AA}, u=0.377$) structure.[23] Nanodots of varying sizes are generated, where we saturate the dangling bonds at the surface with appropriately chosen fractional charge hydrogen atoms (a charge of $0.75e$ or $1.25e$, depending on whether the dangling bond is on a nitrogen or gallium atom, respectively). This ensures that effectively bulk-like GaN bonds are formed, as has been suggested for saturating dangling bonds of semiconductor compounds.[24] The Brillouin zone of the nanodots are sampled at the Γ -point, and we perform full atomic relaxation of all atoms.

We consider nanodots with diameters of 11.0 \AA (94 atoms), 12.5 \AA (132 atoms), 13.3 \AA (156 atoms), 13.7 \AA (168 atoms), 15.2 \AA (228 atoms), 17.7 \AA (342 atoms) and 22.8 \AA (692 atoms). The shapes of nanodots are chosen in such a way as to minimise the number of dangling bonds at the surface, and such that there are the same number of gallium and nitrogen atoms in any particular nanodot. We also tested a number of more “rounded” nanodots which had more dangling bonds at the surface but these were found to be less stable. We note, however, that it is possible there may be other more stable nanodots than those we considered. Illustrations of the nanodots we consider are shown in figure 1.

3. Results and Discussion

We first examine the average Ga-N bond length in each of the nanodots. We find values of $1.940, 1.941, 1.941, 1.942, 1.943$ and 1.945 \AA for the 94, 132, 156, 168, 228, 342 and 692-atom nanodots, respectively. Although the change is small, as the size of the nanodot increases, the average Ga-N bond length increases, approaching the average Ga-N bond length of 1.945 \AA found in bulk wurtzite GaN. We have previously reported similar behaviour for GaN nanowires.[23] Examining the Ga-N bond lengths in more detail, we can analyse how the bond length changes at the surface of the nanodots compared to in the centre of the nanodots. For Ga-N bonds in the $[0001]$ direction, at the surface of the nanodots, there is a contraction of $0.7\text{-}0.9\%$ compared to the bulk Ga-N bond length for all size nanodots, while in the centre there is a contraction of $<0.2\%$. Ga-N bonds also form a zigzag chain perpendicular to the $[0001]$ direction. For

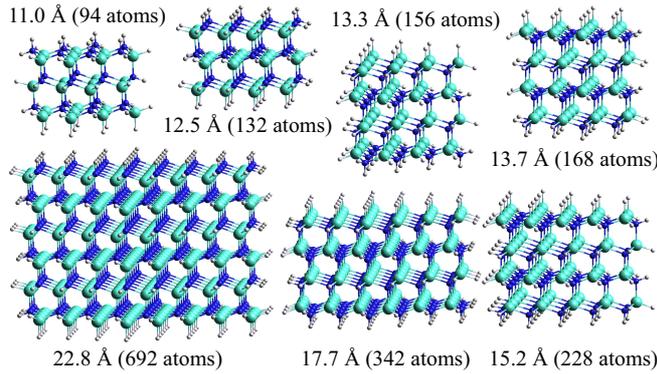


Figure 1. Illustrations of the wurtzite GaN nanodots used in this study. The diameter of each nanodot and the number of atoms (in parenthesis) are also labelled. Nitrogen, gallium and fractional charge hydrogen atoms are indicated by the blue, aqua and small light grey coloured spheres, respectively.

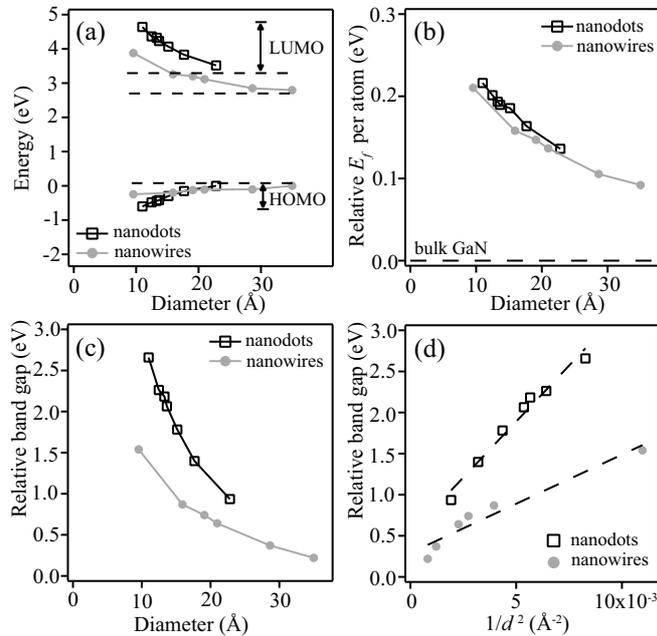


Figure 2. (a) HOMO and LUMO energies as a function of the nanodot and nanowire diameter. (b) Heat of formation (per atom) as a function of diameter. (c) Relative band gap of the nanodots and nanowires as a function of diameter. (d) Relative band gap of the nanodots and nanowires as a function of $1/d^2$, where d is the diameter and the dashed lines indicate the best line of fit to the data. Band gaps are relative to the calculated bulk GaN band gap.

the zigzag chain directions we find similar behaviour to that in the [0001] direction, with a contraction of Ga-N bond lengths at the surface of nanodots of 0.7-0.8 % compared to the bulk Ga-N bond length for all size nanodots, while in the centre the contraction is <0.3%.

We now examine the electronic structure of each nanodot and describe the results in comparison to results from our recent DFT study of GaN nanowires.[25] For each

nanodot, we calculate the energy gap as the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Strictly speaking the electronic structure of nanodots refers to an energy gap and nanowires refers to a band gap, however for the sake of simplicity and clarity, in our following discussion we will refer to both as band gaps. In figure 2(a) we plot the HOMO and LUMO energies for nanodots and nanowires as a function of the diameter. It can be seen that the LUMO exhibits a greater variation than the HOMO over the nanodot sizes examined. In particular, as the nanodot diameter increases from 11.0 Å to 22.8 Å, the shifts of the HOMO and LUMO values are +0.60 and -1.12 eV, respectively. We observe similar behaviour for GaN nanowires, where nanowires with hexagonal shaped cross-sections with diameters ranging from 9.5 Å to 35.0 Å, exhibit shifts of the valence band maximum and conduction band minimum of +0.30 and -1.10 eV, respectively.[25] This suggests that the eigenstates in the conduction band of both nanodots and nanowires are much more sensitive to the diameter. Similar behaviour has been previously reported in tapered silicon nanowires.[26]

We now consider the heat of formation (per atom) of the saturated nanodots and nanowires, using the expression:

$$E_f = \left\{ E [x (\text{GaN}) y\text{H}] - \left[xE (\text{Ga}) + \frac{x}{2}E (\text{N}_2) + \frac{y}{2}E (\text{H}_{\text{sat}}) \right] \right\} / (2x + y) \quad (1)$$

where $E [x (\text{GaN}) y\text{H}]$ is the total energy of the nanodot (or nanowire), $E (\text{Ga})$ is the energy of a gallium atom obtained from the energy of bulk gallium metal, and $E (\text{N}_2)$ is the energy of a nitrogen molecule. In our previous work on nanowires[23] hydrogen atoms were used to saturate dangling bonds, so for nanowires $E (\text{H}_{\text{sat}})$ is the energy of a hydrogen molecule. For nanodots we used fractionally charged hydrogen atoms to saturate dangling bonds, so for nanodots $E (\text{H}_{\text{sat}})$ is the energy of a hydrogen molecule where one of the hydrogen atoms has a fractional charge of $0.75e$ and the other $1.25e$.

The heat of formation (per atom) for the nanodots and nanowires as a function of the diameter is shown in figure 2(b). It can be seen that as the nanodot diameter increases, the relative stability of the nanodot increases, as indicated by the lower heat of formation, approaching the stability of that found in bulk GaN. Similar behaviour is observed for the formation energy of saturated GaN nanowires. It can also be seen that the nanowires are slightly more stable than the nanodots, as may be expected due to the smaller surface regions.

In figure 2(c), figure 2(d) and figure 3 it can be seen that the band gap of the GaN nanodots (relative to the calculated bulk GaN band gap) is larger than that of the nanowires. Also, the variation with diameter is greater for the nanodots. This is consistent with expectations from the simple effective-mass approximation particle-in-a-box (EMA-PIB) model described in the introduction. In figure 2(c) we plot the

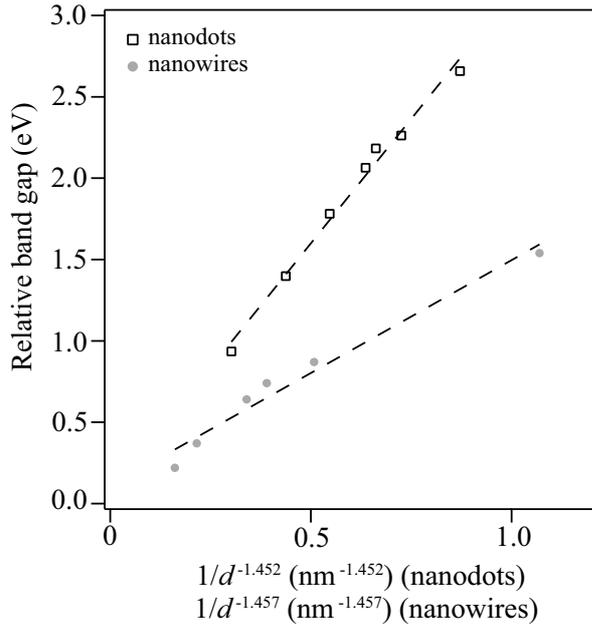


Figure 3. Relative band gap of the nanodots and nanowires as a function of $1/d^x$, where d is the diameter and the dashed lines indicate the best line of fit to the data. Band gaps are relative to the calculated bulk GaN band gap.

relative band gaps of the nanodots and nanowires as a function of the diameter. We find that as the nanodot diameter increases the band gap decreases, approaching that of the band gap of wurtzite bulk GaN. This compares closely with a similar trend found in semi-empirical tight-binding calculations[17] of GaN nanodots. GaN nanowires exhibit a similar behaviour, as we have previously observed.[23] In figure 2(d) we plot the relative band gap as a function of $1/d^2$, with the ratio of the slopes of the lines of best fit for the nanowires and nanodots calculated to be $1.29:2.72 = 0.474$. This ratio can be compared to that obtained for InP nanowires and nanodots of 0.585, from EMA-PIB calculations, and 0.62, from experimental investigations.[27] It should be noted that bands gaps are of course underestimated using DFT-LDA/GGA methods, however our calculations using self-interaction corrected (SIC) pseudopotentials[28] suggest that relative band gaps and associated trends from DFT-LDA/GGA methods compare closely to the results obtained from the more accurate band gaps using the SIC pseudopotential method.

For nanodots and nanowires with small diameters, the contribution of the surface to the electronic properties is not necessarily negligible (compared to the contribution for larger diameters), leading to deviations from the $1/d^2$ proportionality relationship of the EMA-PIB model. Such deviations have been reported for both InP[29] and GaN[23] nanowires. Instead of plotting the relative band gap (i.e. with respect to the bulk band gap) versus $1/d^2$ (figure 2(d)), we fit the results to an equation of the form $\Delta E_g = Ad^x$, as illustrated in figure 3. We find the values of x for the nanowires and nanodots are 1.457 and 1.452, respectively, and for the gradients (A) we find 1.784 and 3.179 respectively, yielding a ratio of the gradients wires:dots equal to 0.561. Comparing this

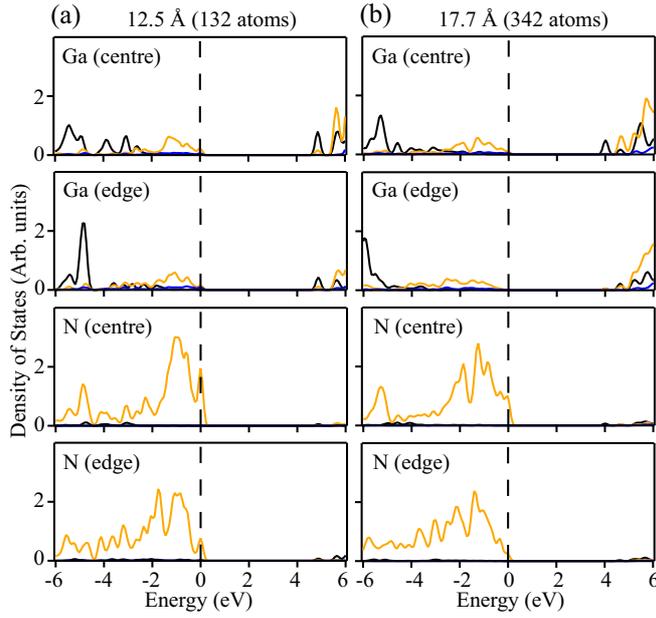


Figure 4. Partial density of states (PDOS) for nanodots with diameters of (a) 12.5 Å (132 atoms) and (b) 17.7 Å (342 atoms). The black, orange and blue lines correspond to s -, p - and d -states, respectively. The energy zero corresponds to the highest occupied state.

to the theoretical studies of GaN nanowires and nanodots by Li and Wang,[18] using a charge patching density functional method combined with band structure corrections, they find values of x for the nanowires and nanodots are 1.15 and 1.32, respectively, and the gradients are 1.57 and 2.75, respectively, producing a ratio of wires:dots gradients of 0.571. Thus we find the ratio of gradients matches closely to the work of Li and Wang,[18] although the value of x for the wires is slightly smaller compared to the dots, whereas we find they are almost identical. In the case of InP nanodots and nanowires, using semiempirical pseudopotential calculations, the values of x are reported to be 1.45 and 1.35 for wires and dots, respectively, with gradients of 2.49 and 3.30, yielding a ratio of gradients wires:dots of 0.75.[27] Based on simple effective mass approximations, where quantum dots are spheres and wires are cylinders, the ratio x of wires:dots is 0.586. This indicates our DFT calculations compare closely to the results expected using simple effective mass considerations.

In figure 4 we show the atom-projected density of states (PDOS) for a “small” (12.5 Å) and “large” (17.7 Å) diameter nanodot. In particular, we consider gallium and nitrogen atoms located at the surface of the nanodots and within the centre of the nanodots for comparison. In figure 4(a) for the “small” nanodot, there is little difference (for either gallium or nitrogen) when comparing the PDOS of an atom located at the centre of the nanodot, to that at the surface of the nanodot. A similar trend is observed in figure 4(b) for the “large” nanodot. There appears to be little difference in PDOS when the nanodot diameter changes from 12.5 Å to 17.7 Å. The PDOS also suggests that the highest occupied states of the nanodots are predominantly the nitrogen $2p$

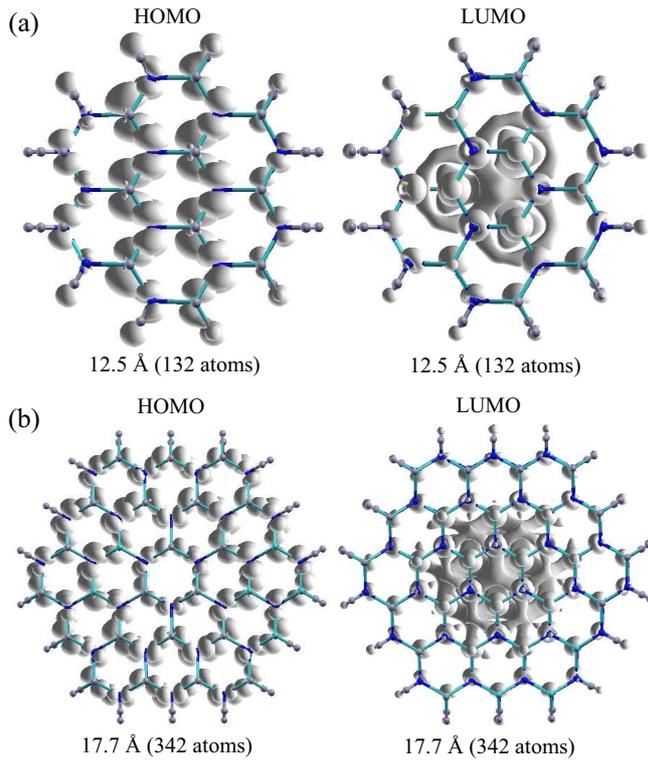


Figure 5. Spatial distribution of the HOMO and LUMO states at the Γ point for nanodots with diameters of (a) 12.5 Å (132 atoms) and (b) 17.7 Å (342 atoms). Nitrogen and gallium atoms are indicated by blue and aqua coloured spheres, respectively, and the orbital states are light grey.

orbitals, while the lowest unoccupied states are contributed by the gallium $3s$ and $3p$ orbitals. We previously observed similar behaviour in saturated GaN nanowires, with the valence band and conduction band edges predominantly dominated by nitrogen $2p$ and gallium $3p$ orbitals, respectively.[23]

Finally, we investigate the spatial distribution of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) at the Γ point for a “small” (12.5 Å) and “large” (17.7 Å) diameter nanodot. This is illustrated in figure 5. In figure 5(a) for the “small” nanodot, the HOMO states mainly form localised regions centred on N atoms, while the LUMO states exhibits some extended delocalised regions, where orbitals appear to connect. Similar behaviour is observed for the “large” diameter nanodot in figure 5(b). Similar localised/delocalised behaviour of the HOMO/LUMO states has been reported previously for hydrogen saturated diamond clusters,[30] though we found no such delocalised behaviour for GaN nanowires.

4. Conclusions

We have examined the atomic and electronic structure and stability of GaN nanodots with diameters ranging from 11.0 to 22.8 Å. For GaN nanodots of all sizes, there is a contraction of Ga-N bond lengths at the surface of the nanodots of 0.7-0.9 % compared

to the bulk Ga-N bond length for all size nanodots considered, while in the centre of the nanodots, the contraction is $<0.3\%$. The average Ga-N bond length in the nanodots increases as diameter increases, approaching the bond length in bulk GaN. Examining the electronic structure, we find that as the nanodot diameter increases, the band gap of the nanodot decreases, approaching that of the band gap of wurtzite bulk GaN. We also observe that eigenstates in the conduction band are more sensitive to the nanodot diameter, than those in the valence band. Furthermore, the relative stability of the nanodot increases (as shown by the lower formation energy) as the diameter increases. Comparing the behaviour of nanodots to nanowires, we find that nanodots exhibit a larger band gap for a given diameter and the variation with diameter is greater, as expected on the basis of simple effective mass particle in a box model, which indicates how quantum confinement should depend on the geometry of confinement. Interestingly, for saturated nanodots, in contrast to nanowires, the lowest unoccupied molecular orbital is found to exhibit a delocalised character, being spread across the centre region of the nanodot.

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